

*April, 1933*

# RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY

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VOLUME VI

NUMBER 2



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# RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division  
of the American Chemical Society,  
20th and Northampton Streets,  
Easton, Pa.

Editor.....C. C. DAVIS  
Associate Editor.....H. L. FISHER  
Secretary-Treasurer.....H. E. SIMMONS

Vol. VI

April, 1933

No. 2

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of \$6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

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# Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

## The Rubber Division of the American Chemical Society

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Executive Committee..E. R. BRIDGWATER, E. B. CURTIS, L. C. PETERSON, A. F. POND, F. W. STAVELY  
Sergeant-at-Arms.....C. W. CHRISTENSEN

## The Spring Meeting of the Rubber Division of the American Chemical Society in Washington, D. C. March 28-29, 1933

The spring meeting of the Rubber Division of the American Chemical Society was held in the Raleigh Hotel in Washington, D. C., March 28 and 29, 1933, with the following program:

### *Tuesday Morning, March 28*

- 9:00 George A. Sackett. The Variability of Rubber from the Plantation View-point.  
9:15 Discussion.  
9:20 A. A. Somerville and W. F. Russell. Low-Sulfur Compounding.  
9:45 Discussion.  
9:55 B. S. Garvey, Jr., W. D. White, and G. Thompson. Soft Vulcanized Rubber—Relation between Combined Sulfur and Vulcanization.  
10:15 Discussion.  
10:35 H. C. Jones. Reactions during Vulcanization. III. The Multiple-Accelerator Effect.  
10:40 Discussion.  
10:45 J. R. Sheppard and W. J. Clapson. Basic Lead Carbonate with Organic Accelerators in the Vulcanization of Rubber.  
11:00 Discussion.  
11:05 W. A. Gibbons, R. H. Gerke, and H. C. Tingey. The T-50 Test for State of Cure.  
11:25 Discussion.

### *Tuesday Evening, March 28*

#### Joint dinner with the Paint and Varnish Division

- 9:00 Frank H. Roninger, Jr. A Method for the Microscopic Examination of Rubber and Other Solid Technical Products.  
9:15 Discussion.  
9:20 Raymond P. Allen and Frank K. Schoenfeld. Dispersibility of Gas Black. I. Methods of Measuring Gas Black Dispersion.  
9:35 Discussion.

- 9:45 Frank K. Schoenfeld and Raymond P. Allen. Dispersibility of Gas Black.  
II. Evaluation of Gas Blacks.  
10:05 Discussion.  
10:15 M. K. Easley. The Effect of Acicular Zinc Oxide on the Physical Properties of a Rubber Compound.  
10:30 Discussion.  
10:35 Bernard L. Johnson and Frank K. Cameron. The Mechanism of the Aging of Rubber.  
10:50 Discussion.  
11:00 Business Meeting.

One hundred twenty-five men attended the two sessions of the Division.

At the business meeting held on Wednesday the Division indulged in a general discussion of Fundamental Research. The particular theme of this discussion centered around the fact that the universities of the United States should be encouraged to start more research in the field of rubber, and it was pointed out that this could be done if the industry would help start this work in a financial way.

Some discussion was heard in regard to the Fall Meeting in Chicago, and it was voted that the Committee be appointed to formulate a program on New Physical Methods for Examination of Rubber.

### Report of Secretary

Total paid membership to date.....	344
Regular members.....	257
Associate members.....	74
New members.....	13
Unpaid members.....	100
Unpaid associate members.....	30
Paid subscriptions.....	66
Unpaid subscriptions.....	30
Honorary members.....	31
Cancelled subscriptions or memberships for 1933	11

The meeting of the Executive Committee was held on March 29, 1933, with the following members present: Ira Williams, E. B. Curtis, C. W. Christensen, L. B. Sebrell, E. R. Bridgwater, H. E. Simmons.

The Executive Committee considered the question of the Fall Meeting in Chicago. It was decided that there should be four sessions, with a banquet on Wednesday night. The Secretary was instructed to ask Secretary Parsons for four sessions—two on Tuesday, one on Wednesday morning, and one on Thursday morning. On further discussion it was decided that there should perhaps be invitational papers on five general subjects, as follow:

1. Structure and Nature of Rubber.
2. Vulcanization and Its Nature (Chemical and Physical).
3. Pigmentation.
4. Electrical Properties.
5. Aging.

The Chairman of the Division, L. B. Sebrell, volunteered to line up these subjects and invite different persons to present papers on these sections.

The Rubber Division banquet was held Tuesday evening, March 28, in conjunction with the Paint and Varnish Division in the ball room of the Mayflower Hotel. The Committee on Arrangements are to be congratulated upon the fine program which they furnished and the after dinner speech by Frederick Weil.

One hundred fifty-eight members attended the banquet.

H. E. SIMMONS, *Secretary-Treasurer*

### **The Rubber Exhibition at Cologne**

Beginning June 2, 1933, will be an attempt to depict for the first time the historical development of rubber production and manufacture over the whole world. Commencing with the primitive production and manufacture carried on by the Brazilian natives and the establishment and development of the East Asiatic plantations, the exhibition will follow up the increasing manufacture and application of rubber to the point which this most important industry has reached today. Manufacturing methods in actual progress and exhibits of raw materials and half-finished manufactures necessary for rubber manufactures will be supplemented by exhibits of all the finished rubber manufactures found on the market.

The Rubber Exhibition will be held in the section of the Cologne municipal exhibition buildings, in the Rhine Park, known as the "Houses of the States." This section contains light and roomy halls which will give all exhibitors, both German and foreign, an excellent opportunity for staging impressive displays of every branch. The "Houses of the States" are so constructed that the exhibition can be conveniently divided into two groups, "Production" and "Manufacturing." The "Production" group will embrace the history of rubber up to the modern plantation. It will also include the transport, packing, and shipping of the raw product. In the group "Manufacturing," specialized machinery, raw materials, and finished goods will be shown. A supplementary section will be devoted to "research methods" and especially to manufacturing in progress.

The Chairman of the German Rubber Association, Herr Professor Dr. E. A. Hauser, of Frankfort-on-Main, is acting as technical adviser to the exhibition authorities. The Messe- und Ausstellungs-G. m. b. H., Messeplatz, Deutz, Cologne, is responsible for the organization of the exhibition.

Enquiries should be addressed to Messe- und Ausstellungs G. m. b. H., Messeplatz, Deutz, Cologne. Telegraphic address: Messeamt Cologne.

## Corrections

"The Influence of Temperature on the Evolution of Hydrogen Sulfide from Vulcanized Rubber," by A. D. Cummings, RUBBER CHEMISTRY AND TECHNOLOGY, Volume 6, page 53, January, 1933.

The original article published in the Bureau of Standards *Journal of Research*, Volume 9, pages 163-174, August, 1932, contained in Table II on page 172, an error in the percentage of residual rubber after decomposition by heat. The value in the original article was 95.55 per cent, whereas the correct value is 97.55. An attempt to correct the total value in RUBBER CHEMISTRY AND TECHNOLOGY introduced a different error. The table should read as follows:

TABLE II  
PERCENTAGE OF ORIGINAL SAMPLE ACCOUNTED FOR AFTER A 32 PER CENT COMPOUND  
WAS HEATED 200 HOURS AT 136° C.

	Per cent
Residual rubber	97.55
Oils	0.01
Sulfur	0.02
Moisture	0.18
Hydrogen sulfide	2.17
Total	99.93

\* \* \* \* \*

"Compression Stress-Strain of Rubber," by Sheppard and Clapson, RUBBER CHEMISTRY AND TECHNOLOGY, Volume 6, page 130, January, 1933.

In the original article in *Industrial and Engineering Chemistry*, Volume 24, pages 782-790, July, 1932, and in its reprint in RUBBER CHEMISTRY AND TECHNOLOGY, there is an error. The paragraph beginning "Equation 4 defines ...; Equation 5 defines ..." should read as follows:

"Equation 5 defines the compressive force as a function of the equivalent tensile and of the new (diminished) length in the direction of compression when the original (unstrained) specimen is a cube of unit length; Equation 4 defines the compressive force in terms of the equivalent tensile ...."



## New Books and Other Publications

**Rubber Latex.** Henry P. and W. H. Stevens. Issued by The Rubber Growers' Association, Inc., 2, 3, and 4 Idol Lane, Eastcheap, London, E. C. 3, England. Paper, 155 pp. 5½ by 8½ inches. Illustrated.

This is a revised and enlarged edition of the work by the same authors, first issued July, 1928. The book deals with the properties, composition, coagulation, concentration, manipulation, and compounding of latex and latex pastes and its stabilization for industrial purposes. The vulcanization of latex and latex products, dipping, electro-deposition, and the marketing and applications of latex are also discussed. A final chapter deals with a selected list of over 500 recent British patents and testifies to the growing importance which is attached to the direct application of latex. An index to the text and to the patents, together with a very full bibliography of books of reference and literature are included and should prove very useful to latex users. [From the *India Rubber World*.]

**Latex and Its Industrial Applications.** By Frederick Marchionna, published by *The Rubber Age*, 250 West 57th St., New York City. Cloth bound, 1060 pp., 6 by 9¼ in. Price, \$15.00 postpaid.

This new volume is a welcome addition to the technical literature on latex inasmuch as it treats this subject in a more detailed and comprehensive manner than any other work available. The book is especially timely as interest in latex is greater today than ever before—not only in the rubber industry but also in many fields not heretofore users of rubber in any form.

With the direct use of latex increasing rapidly, there has become apparent a need for a bibliography which would gather together all the more important patents on this subject as well as a résumé of the published literature. Much of this information is not readily available to the research worker and to many of the rubber companies and accordingly this new book serves to bring together for the first time all the essential literature on this subject.

The compiler of this bibliography, while working in the United States Patent Office, has had occasion to observe the great need for an exhaustive work on latex and its uses. Since there are several good books on the market, such as "Estate Rubber—Its Properties and Testing," by Dr. O. de Vries; Professor G. S. Whitby's excellent monograph, "Plantation Rubber and Testing of Rubber;" B. D. Luff's "The Chemistry of Rubber;" L. E. Weber's "The Chemistry of Rubber Manufacture;" Dr. P. Schidrowitz's "Rubber;" Gottlob's "Technology of Rubber;" Dr. E. A. Hauser's "Latex," and others, a greater need has been felt for a bibliographic work in which all the investigations and researches which have been carried out on latex from the plant to the manufacture of rubber products, all the practical applications in the direct use of latex, as described in patents, are briefly, clearly, and succinctly abstracted.

Thus was born the idea to supply this need, and the work has been facilitated by the well supplied libraries in the Government Departments of the Patent Office, Bureau of Standards, Bureau of Chemistry, Department of Agriculture, and the Library of Congress.

These abstracts include the technical literature involving plantation, collection, coagulation, concentration, vulcanization, and direct use of latex. It has been thought better to cover fully the use of Hevea latex and, only incidentally, other types of latices so as to bring out the comparison between the behavior and properties of latices from various rubber-bearing plants.

Contact at the Patent Office with the patent and technical literature of the



world led the author to conclude that in the field of rubber technology—industrial applications of rubber—there are four nations which dominate the field: United States, England, France, and Germany. Any important patent from another country is certain to be duplicated in some corresponding patent granted in any or all of the four named countries. In the German edition of Dr. E. A. Hauser's "Latex," Dr. Carl Boehm Von Boernegg, in compiling a short bibliography of patents on latex, made the statement that England, Germany, and France predominate in the field of patent development on latex and rubber; none of the United States patents were included in this short bibliography. The compiler of this work, however, has found that the United States leads all the other countries in the field of patents on latex and its industrial applications.

In abstracting the articles in technical journals and the patents, the compiler has had in mind briefness, thoroughness, and lucidity. Attention has particularly been paid to original research done by scientists advancing new theories, new concepts in the field of application of the new physics and chemistry to rubber. Careful attention has been given to the present trend in the industrial application of latex, so that in the abstracts not only the process and apparatus have been described, but also the intended purpose and use have been brought out. This has been done for the purpose of enabling scientists, inventors, industrials, technical men, etc., to derive the greatest possible advantages and benefits from the reading of the book, without the necessity of consulting the original source if it is not readily available.

The bibliographic work has been arranged in chapters to facilitate the search for a particular subject. The literature has been placed after the patents for each particular subject, since the technical articles are, in several instances, criticisms of certain patent developments, or reports of investigations on the value of certain patented processes or machines. The abstracts are unbiased; they merely state in brief what has been described or said without making any personal critical comment. [From *The Rubber Age* of New York.]

**A.S.T.M. Tentative Standards 1932.** American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Cloth or heavy paper, 1236 pp., 6 by 9 inches. Indexed.

The 1932 edition of this handbook contains all of the 226 tentative standards of the Society. The term "tentative" is applied to a proposed standard which is to be published and distributed to elicit comments and criticism from all interested parties. Because of their careful promulgation by the A.S.T.M. committees and subsequent critical examination by the Society before publication, A.S.T.M. tentative standards are widely used in industry. Specifications adopted this year are given for insulated wire and cable, performance rubber compound, and tolerances and test methods for tubular sleeving and braids. Besides the tentative standards the book includes proposed revision of standards published as tentative before final action is taken. [From the *India Rubber World*.]

**Proceedings of the Thirty-fifth Annual Meeting.** Held at Atlantic City, N. J., June 20-24, 1932. Vol. 32. American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Cloth. Illustrated. Subject and author indices. Part I has 1071 pp.; Part II, 824 pp. Price for each part, \$5.50, paper binding; \$6.00, cloth; \$7.00, half-leather.

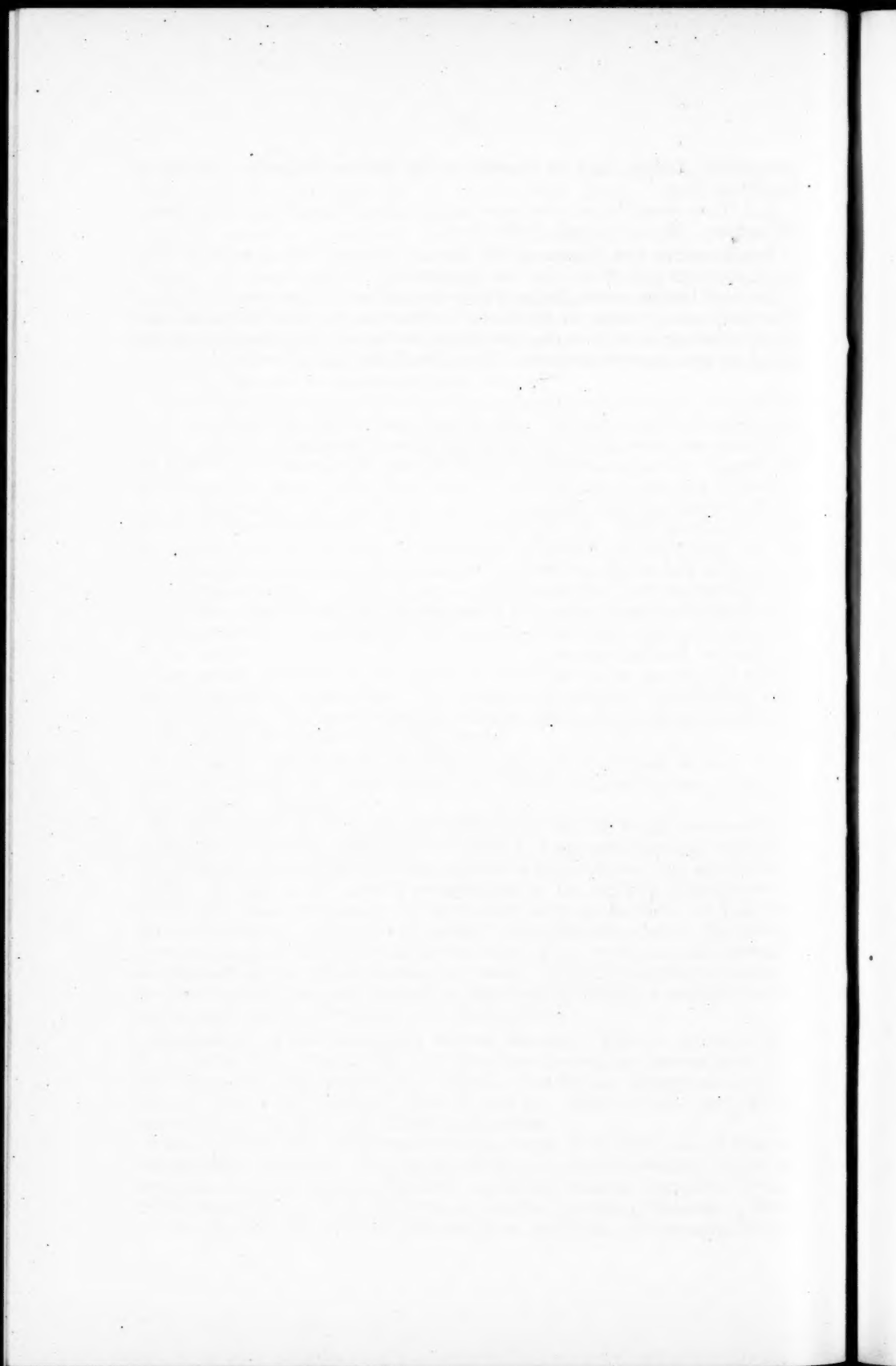
Part I contains the annual reports of the Society Committees and the papers and standards appended. Rubber manufacturers and technologists will be interested in the report of Committee D-11 on Rubber Products, Committee D-13 on Textile Materials, and Committee D-9 on Electrical Insulating Materials. Tentative specifications are given on Insulated Wire and Cable; Performance Rubber

Compound; Friction Tape for General Use for Electrical Purposes; and Rubber Insulating Tape.

Part II comprises the technical papers given at the thirty-fifth annual meeting of the society. [From the *India Rubber World*.]

**The Romance and Drama of the Rubber Industry.** By Harvey S. Firestone, Jr. 128 pp., 1933. For free distribution.

The book contains a compilation of fifty-one talks recently given on the "Voice of Firestone" radio program, by Mr. Harvey S. Firestone, Jr. One will find it helpful in any reference work concerning the history and facts of the rubber industry and full of the romance of the industry. [From *The Rubber Age* of New York.]



# The Problem of Changes in Rubber Brought About by Atmospheric Oxygen

Charles Dufraisse

L'ÉCOLE DE PHYSIQUE ET DE CHIMIE INDUSTRIELLES, PARIS, FRANCE

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    - Interpretation of the phenomena
    - Conclusions

Various recent publications in different countries have called the attention of technologists to the attack of rubber by atmospheric oxygen, a reaction the importance of which has perhaps not yet received proper recognition.

The object of the following pages is to review the principal experimental facts and to discuss their importance. Since oxidation by oxidizing agents is a phenomenon of an entirely different nature from that by free oxygen, it has no place in this study and it will not be discussed here. On the other hand because of its relations with the phenomena of autooxidation the action of ozone will in a few exceptional cases be considered from this particular point of view, which is distinct from the work of Harries and his school.



point a molecule like that of rubber, which has an accumulation of ethylenic bonds to the extent of one for every four groups, is open to attack by an oxidizing agent.

As a matter of fact, as a result of various disturbing factors (a particular physical state, and above all impurities), it is difficult to form an exact idea in the case of rubber itself of the extent to which the molecules are rendered oxidizable by such a massing of double bonds. To settle this question it is necessary to turn to another substance, chemically similar but with which it is easier to avoid difficulties leading to errors, and above all in which there are no impurities.

No product meets these requirements better than does the natural terpene, limonene, because of its close relationship to rubber. It has the same percentage composition, *i. e.*, the same empirical formula  $(C_5H_8)_n$ , where  $n$  is 2. As the formula in Fig. 1 shows, this also has as many double bonds as the isoprene molecule. Finally, it has the same genetic relations to the base parent hydrocarbon, isoprene, as does rubber itself, for it is formed from isoprene by condensation, and it again gives isoprene by thermal dissociation.

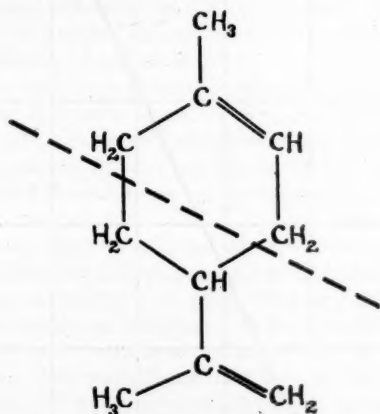


Figure 1—Formula of Limonene, Containing Two Isoprene Molecules and Two Ethylenic Bonds. The Broken Line Separates the Two Isoprene Molecules

In view of such important similarities, it is instructive to know the behavior of limonene toward oxygen. When pure limonene is brought into contact with pure oxygen, it absorbs this gas at a rate which is indicated by the curve in Fig. 2,<sup>5</sup> where the abscissa represents the time and the ordinate represents the oxygen consumed as percentages by weight. After a short period of induction, limonene is oxidized in darkness at a rate of 0.3 per cent per 24 hours.

If rubber were to be oxidized at this rate, it would become useless in a day. It is very fortunate that its tendency to oxidize is less than this, and moreover that it varies according to circumstances. As a matter of fact, because of its structure alone, rubber is exposed to active oxidation. As a rule this reactivity is very seldom apparent, but this is merely because it is dormant, and it sometimes awakens with disturbing results so that it is necessary always to be on the alert.

#### Historical

Contrary to the impression which one might receive from these theoretical considerations, the action of oxygen has been misunderstood for a long time, and it was



scarcely twenty years ago that any serious attempt was made to study the subject.

If this is no longer true today, it has not been accomplished without opposition, and even at the present time there are some who tend to doubt either the reality or at least the importance of the part played by oxygen.

This state of mind is accounted for by the difficulties in the experimental technique, which will be described in detail further on; they have been overlooked by certain investigators, whose erroneous conclusions have as a result thrown their ideas into confusion and have led to scepticism.

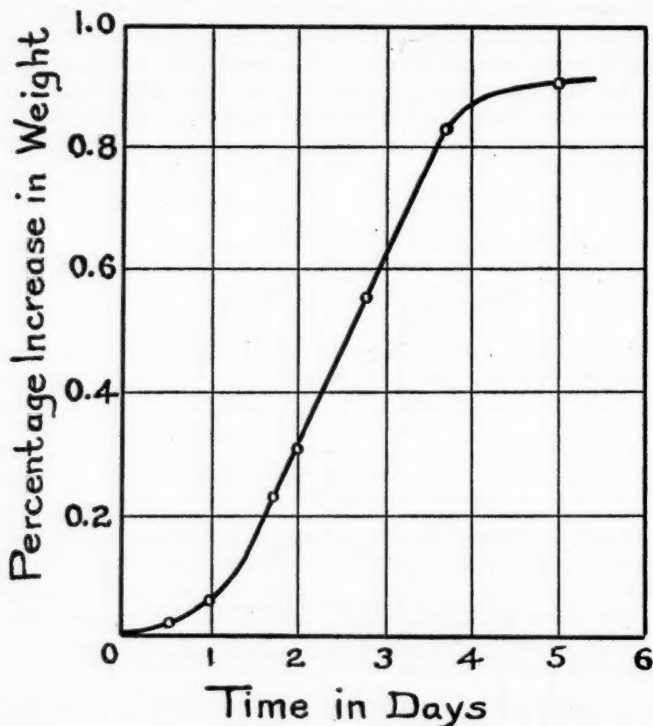


Figure 2—Oxidation of Limonene in Pure Oxygen. Percentage by Weight of Oxygen Absorbed as a Function of the Time  
(This diagram is based upon experiments by Dufraisse and Drisch<sup>142</sup>.)

This makes it all the more interesting and instructive to follow the progress of truth to final victory through the numerous publications on this subject.

Since the authors who have already covered the historical phase have frequently confined themselves to a small number of references, I believe it will be of service to the reader to give first of all, in a chronological order with a word about the general significance of each work, a list of publications which have contributed most directly to establish this branch of science. It will at the same time do justice to a certain number of works which are only too frequently left in unmerited oblivion. A more detailed review will be made in the subsequent sections.

The first paper to be cited does not deal specifically with rubber, but with the closely related substance, gutta-percha. Hofmann<sup>1</sup> in 1861 in fact proved that



deteriorated gutta-percha is in an oxidized state; he included an analysis of the product and attributed the alteration to oxidation. A comparable work, but dealing with rubber, was carried out by Spiller<sup>2</sup> in 1865, while Miller<sup>3</sup> also in 1865 found an increase in the weight of the two substances during their deterioration, and he too definitely concluded that atmospheric oxygen was the harmful agent.

After such a beginning knowledge should have progressed rapidly, but such was not the case. However explicit this knowledge may have been, these first publications have been disregarded. In any case, there was silence for nearly twenty years, which was broken by Burghardt<sup>4</sup> in 1883, who connected the rate of deterioration with the quantity of oxygen consumed. In addition he pointed out the accelerating action of light. The first direct proof of the harmfulness of oxygen is due to Thomson<sup>5</sup> in 1885, who showed that in an inert gas or in a vacuum there is no alteration, provided the technique is correct. This experiment was decisive, but on account of the experimental difficulties mentioned earlier and which will be considered later, it has not received the importance it deserves. Still others who have undertaken to study with insufficient technique, in spite of warnings by Thomson himself, had no success, and they felt justified in denying the influence of oxygen, causing confusion which it was difficult to overcome later.

While studying the reactions of metals and metallic salts the same author, at first alone in 1890<sup>6</sup> and then with Lewis<sup>7</sup> in 1891, introduced the method of oxidation accelerated by heat at moderate temperature (66° C.). This was the basis of a practical method of testing which Geer was to find so successful later. Vladimiroff<sup>8</sup> in 1892 worked in the same way by heating his samples in an air bath but at an appreciably higher temperature (125° C.). The same thought inspired Henriques,<sup>9</sup> who in 1895 used light as well, and proved that there was a gain in weight.

C. O. Weber<sup>10</sup> in 1900 called attention to the strong tendency to oxidize which is manifest upon drying, especially with heat. Ramsay, Chick and Collingridge<sup>11</sup> in 1902 oxidized gutta-percha in solution. C. O. Weber<sup>12,213</sup> in 1903 pointed out the destructive action, which was slow but noticeable, of air upon manufactured products. Herbst<sup>13</sup> in 1906 carried out oxidation in solution and analyzed the products formed. Ditmar<sup>14</sup> went on record in 1906 in favor of the theory of oxidation, and he recommended a stability test which consisted of determining the increase in weight resulting from heating to 100° C. in oxygen; in 1907<sup>15</sup> he recognized the accelerating influence of too high a temperature of vulcanization.

Much had been written to overestimate the part played by microorganisms up to the time when Bertrand<sup>16</sup> in 1908 rendered the great service of properly evaluating atmospheric agents, particularly light, which Raybaud<sup>17</sup> emphasized later in 1909 in connection with solar ultra-violet radiation. Heil and Esch<sup>18</sup> in 1909 attributed the deterioration of vulcanized rubber to oxidation, but not the formation of fatty substances in raw rubber. They also called attention to the glazing effect caused by heat and light. In 1910 Henry<sup>19</sup> observed the pronounced effect of ultra-violet radiation, provided that oxygen is present. In 1910 Ahrens<sup>20</sup> showed in an excellent way the accelerating power of light on the oxidation of raw rubber and the resulting stickiness. He reproduced this photographically by exposing a fresh surface to sunlight behind a negative, where the most highly oxidized and stickier portions correspond to the white portion of the plate. He showed this by dusting the plate with pollen.

After Spiller and Thomson, Fickendey<sup>21</sup> (1911) is one of the most prominent names among the earlier workers on the autooxidation of rubber, because of the clearness with which he recognized and proved the influence of oxygen on this change.

In 1912 Peachey<sup>22</sup> published the first of the remarkable works which were to appear from him and his collaborators on oxidation carried to its extreme limit. He explained the chief characteristics and determined the maximum quantity of oxygen absorbed. According to Gorter<sup>23</sup> in 1912, light and heat cause stickiness only in the presence of oxygen. Wo. Ostwald<sup>24</sup> in 1913 showed that, as judged by the curves of Peachey, oxidation follows an autocatalytic course, or in terms used so frequently at the present time there is a period of induction. Peachey<sup>25</sup> in 1913 discussed the subject further. In 1913 Ahrens<sup>26</sup> presented new facts upon oxidation in the presence of solar and ultra-violet radiation, and he considered the possibility of a catalytic action. Kirchhof<sup>27</sup> in 1913 oxidized raw and vulcanized rubber with heat and cold and showed that intermediate peroxides were formed. Whitby<sup>28</sup> in 1913 described some exceptionally severe cases of deterioration by oxidation. In 1913 van Rossem<sup>29</sup> refuted a theory which attempted to compare stickiness to a spontaneous rearrangement after fusion of the nature of "tin pest."

Kirchhof<sup>30</sup> in 1914 compared the addition reactions with oxygen, bromine and sulfur chloride. Van Rossem<sup>31</sup> in 1914 described a considerable deteriorating effect which began with the first appearance of oxidation, and he used the expression catalysis outright. In 1915 Gorter<sup>32</sup> again showed by the manometric method the absorption of oxygen and the stickiness which accompanies it. Geer<sup>33</sup> in 1916 published his method for accelerated aging in the oven which is now very widely used. In 1916 Stevens<sup>34</sup> began the publication of his classic studies on the degree of vulcanization and the relation between this rate of vulcanization and the rate of deterioration. Peachey and Leon<sup>35</sup> in 1918 continued the earlier work of Peachey himself, and determined particularly the limit of oxidation. Van Rossem<sup>36</sup> in 1918 studied the influence of heat and of light on mastication. In a series of four papers in 1918 and 1919 Stevens<sup>37, 38, 39, 40</sup> published the results of his work on the tendency of rubber to deteriorate and the relation of this change to the degree of vulcanization. In 1919 Repony<sup>41</sup> pointed out the failure in industrial practice to exclude air and light. Eaton and Day<sup>42</sup> in 1919 observed the increase in weight which accompanies deterioration, confining themselves to the case of highly vulcanized rubber. Stevens<sup>43, 44</sup> in 1920 continued the publication of his investigations. Kirchhof<sup>45</sup> in 1920 advanced hypotheses upon the possible effect of the sulfuric acid which is formed by the oxidation of sulfur. In 1920 Porritt<sup>46</sup> experimented with light and gave his results in a brief but comprehensive paper where the role of oxygen was examined from the historical, theoretical, and practical points of view. These few pages should be regarded as marking the beginning of a new phase of our knowledge of the subject. Since that time, papers of a more and more precise nature have accumulated rapidly.

Geer and Evans<sup>47</sup> in 1921 published a summary of results which they had previously obtained upon oxidation with heat. King<sup>48</sup> in 1921 summarized results obtained by various investigators on the phenomenon of autooxidation and its effects. Tuttle<sup>49</sup> in 1921 emphasized the fact that light promotes oxidation, and he verified the fact that the reaction is autocatalytic. In 1921 Bruni and Pelizzola<sup>50</sup> described the activating power of manganese, and they studied the presence of this metal in rubber. Asano<sup>51</sup> in 1922 oxidized raw rubber with heat and with light. Evans<sup>52</sup> in 1922 studied heat in a new way. Pelizzola<sup>53, 54</sup> in 1922 compared natural and artificial aging from the physical and chemical points of view. According to Bruni and Pelizzola<sup>55</sup> the stickiness of raw rubber and the deterioration of vulcanized rubber are oxidation processes, and they suggested in 1922 that they were chemical reactions. When rubber deteriorates, aldehydic substances are formed, and their presence was detected by Kaye<sup>56</sup> in 1922 and also characterized by Whitby<sup>57</sup> in 1922. Boswell, Hambleton, Parker, and McLaughlin<sup>58</sup> in 1922

analyzed the products of oxidation. In 1922 Bruni<sup>59</sup> measured the volume of oxygen consumed in a sealed tube after ten days. Marx and Zimmermann<sup>60</sup> in 1922 tested the resistance of *Manihot* rubber to sunlight and to heat. They reviewed the effects of the mode of coagulation and factors involved in the gathering of the latex and the subsequent operations. Pummerer and Burkhard<sup>61</sup> in 1922 determined the limit of saturation in a dilute liquid. In 1922 Kirchhof<sup>62</sup> developed a theory according to which sulfuric acid would be the active intermediate agent. Marzetti<sup>63</sup> in 1923 followed the rate at 77° C. by measuring the volume of gas. Bierer and Davis<sup>64</sup> published in 1924 their fundamental study on the effect of pressure, and developed from this their well-known practical method, the first applications of which were described. Few publications have received the same attention from technologists. They have done the most to spread and to popularize correct ideas concerning the true cause of alteration, *i. e.*, oxygen.

In 1925 Peritor<sup>65</sup> studied the tendency to oxidize by the sensitivity to ozone. Asano<sup>66</sup> in 1925 irradiated rubber with sunlight and ultra-violet radiations of high frequency. He compared the deterioration with and without oxygen.

Bierer and Davis<sup>67</sup> in 1925 by further experiments strengthened their opinion that air is chiefly responsible for the spontaneous perishing of rubber. At the same time (1925) and by comparing several methods, other investigators reached a similar conclusion, including Morron and Webster,<sup>68</sup> Thomson,<sup>69</sup> Somerville,<sup>70</sup> Glancy,<sup>71</sup> Vogt,<sup>72</sup> Winkelmann,<sup>73</sup> and Jones.<sup>74</sup> This last investigator showed once more that rubber is stable in the absence of oxygen.

In the course of a general study upon autooxidation and the catalytic reactions which are associated with it, Moureu and Dufraisse<sup>75</sup> in 1925 published a general theory with new points of view on oxidation by free oxygen, on the peroxides which are formed as a result of this oxidation, and on the ultimate fate of these peroxides and their complicated reactions. Known since as the theory of peroxides, it has been adopted by most specialists of autooxidation to explain the extremely complicated reactions occurring during the alteration of oxidizable substances, among the most important of which is rubber.

Van Rossem and Dekker<sup>76</sup> in 1926 described the behavior of certain metals and acids with the non-rubber substances. Shepard, Krall, and Morris,<sup>77</sup> as well as Morris alone,<sup>78</sup> in 1926, examined the different types of surface attack and the way they depend upon such factors as light and stretching. In 1926 Park<sup>79</sup> compared several types of deterioration. Jecusco<sup>80</sup> in 1926 determined the relative activities of different radiations from infra-red to ultra-violet, both cold and hot. Boggs and Follansbee<sup>81</sup> in 1926 found that rubber vulcanized with selenium is less easily altered than when vulcanized with sulfur. In 1926 Williams<sup>82</sup> made oxygen react in the presence of light, paying particular attention to surface deterioration. L. E. Weber<sup>83</sup> in 1926 presented a critical review of the subject and some original views of his own. Staudinger and Geiger<sup>84</sup> in 1926 observed a lowering of the softening temperature and of the viscosity in the presence of oxygen. Dawson and Porritt<sup>85</sup> in 1927 oxidized balata. Martin<sup>86</sup> in 1927 compared the different commercial forms of plantation rubber. He likewise investigated the influence of the degree of vulcanization. In 1927 Krah<sup>87</sup> studied the effect of ultra-violet radiation and ozone, Kirchhof<sup>88,89</sup> ultra-violet radiation, heat and metallic salts, and Fry and Porritt<sup>90</sup> heat alone. The publication of the latter investigators should be mentioned as the forerunner of recent works on mastication. Bierer and Davis<sup>91</sup> in 1927 continued their studies with the bomb in a systematic way. Leon and Lister<sup>92</sup> in 1927 continued the experiments of Peachey and Leon with particular attention to the origin of the rubber, to mastication, to the degree of purity, and to the method of vulcanization. Tener, Smith, and Holt<sup>93</sup> made a very careful study from the

theoretical and practical points of view. They showed once more the necessity of the presence of oxygen, activated by light and heat, and lastly studied the subject of surface brittleness and cracking.

In 1927 and 1928 photooxidation was studied thoroughly by Yamazaki<sup>94,95,96</sup> with solar radiation, and by Weightman<sup>97</sup> with artificial radiation, but with care being taken to reproduce natural conditions. Georgi<sup>98</sup> in 1928 as well as Taylor and Jones<sup>99</sup> studied the influence of different metallic salts, while Dinsmore and Vogt<sup>100</sup> in 1928 reviewed the influence of accelerators of vulcanization. Kelly, Taylor, and Jones<sup>101</sup> in 1928 deteriorated rubber while it was stretched in the same way as was done by Haushalter, Jones, and Schade,<sup>102</sup> who in 1928 also studied the attack of rubber by ozone. Park, Carson, and Sebrell<sup>103</sup> in 1928 compared the plasticization of rubber by heat and by mastication. McKee and Depew<sup>104</sup> in 1928 examined several factors, such as humidity, tension, etc. In 1928 Fol and de Visser<sup>105</sup> reported that spontaneous combustion might take place in the presence of copper.

In 1929 Yamazaki and Okuyama<sup>106</sup> oxidized at 70° C. rubber which had been extracted with acetone, and then studied the condition of the sulfur. Garner<sup>107</sup> in 1929 exposed raw rubber, both solid and in solution, to ultra-violet radiation. Stevens<sup>108</sup> in 1929 devised a method for testing sponge rubber in the oven. Van Rossem and Dekker<sup>109</sup> in 1929 recommended a determination with alcoholic potassium hydroxide extract for detecting the very beginning of aging. Pummerer<sup>110</sup> in 1929 thought that the decrease in the viscosity of solutions might be due to traces of oxygen. Bierer and Davis<sup>111</sup> in 1929 published new results on deterioration accelerated by compressed oxygen, and compared the results with those obtained in hot air (Geer oven) and at room temperature. The same subject was treated by Krall,<sup>112</sup> Follansbee,<sup>113</sup> Soule,<sup>114</sup> Vogt,<sup>115</sup> Cadwell,<sup>116</sup> and finally by Nellen and Sellers,<sup>117</sup> all in 1929. Davey<sup>118</sup> in 1929 carried out oxidation at 70° C., and studied the way in which the rate of oxidation varies with such factors as the degree of vulcanization, an accelerator (diphenylguanidine), and lastly with the acetone and chloroform extracts. Reed<sup>119</sup> in 1929 considered it still necessary to prove once more that rubber deteriorates when hot only in the presence of oxygen. He stated that traces of this gas are sufficient. To Kohman<sup>120</sup> is to be credited an extensive and careful work on oxidation measured volumetrically. Scott<sup>121</sup> in 1929 examined from the point of view of positive catalysis some ferrocyanides and in particular Prussian and French blues. He also proved that stickiness and resinification are the result of air. Somerville, Ball, and Cope<sup>122</sup> in 1929 determined the effect of stretching. Kirchhof<sup>123</sup> in 1929 showed by means of a photographic method the way in which oxidation extends into the interior.

In 1930 Davey<sup>124</sup> continued his earlier experiments by operating at 100° C. and at room temperature, both in darkness and in light. Temple, Cadwell, and Mead<sup>125</sup> in 1930 made a quantitative study, limited to the first stages. Kearsley<sup>127</sup> in 1930 investigated the characteristics of deterioration brought about by ozonized oxygen. Somerville<sup>128</sup> in 1930 oxidized stretched rubber and<sup>129</sup> discussed tests made upon rubber. Grenquist<sup>130</sup> in 1930 observed the influence of oxidation on the degradation of rubber by mixing, heating, and light. Shacklock<sup>131</sup> in 1930 showed that a moderate degree of oxidation does not change the surface tension. Williams and Neal<sup>132</sup> in 1930 measured the solubility of oxygen, as well as the rate of diffusion and combination as a function of the temperature and pressure. Staudinger and Leupold<sup>133</sup> showed in 1930 the extreme sensitivity of solutions to traces of oxygen. Evans<sup>134</sup> in 1930 made comparative tests by exposing samples to the air and behind the glass of an enclosure in order to observe the appearance of cracks. Yamazaki and Okuyama<sup>135</sup> in 1930 published a work on the increase in



the weight of the acetone extract. Graffe<sup>136</sup> in 1931 studied the most active wave lengths and found them in the ultra-violet region.

Dufraisse and Drisch<sup>137</sup> in 1931 published the first results of a systematic study of different influences, catalytic and otherwise. Kemp, Bishop, and Lasselle<sup>138</sup> made in 1931 a comprehensive study of oxidation and the resulting products in the case of rubber, gutta-percha, and balata. Van Rossem and Talen<sup>139</sup> in 1931 distinguished the part played by each of the atmospheric agents (light, oxygen, and ozone) in the formation of cracks and in surface hardening. Metallic impurities were the subject of a work by Kirchhof<sup>140</sup> in 1931. Staudinger and Bondy<sup>141</sup> reported in 1931 the considerable influence of oxygen, particularly upon the ease of solution and upon the viscosity. Cotton<sup>142</sup> in 1931 studied oxidation and its effects during mastication. Dufraisse and Drisch<sup>143</sup> in 1931 proved that litharge, contrary to common belief, is a pro-oxygen. Shacklock<sup>144,145</sup> in 1931 and 1932 studied the effects of oxygen on some physical properties.

Busse<sup>146</sup> in 1932 studied oxidation and its effects during mastication. In 1932 Booth<sup>147</sup> carried out oxidation at 121° C. in compressed air. A subject of controversy, the influence of temperature and vulcanization on the rate of aging, has been enriched by the bibliographic and experimental work of Shepard and Street<sup>148</sup> in 1932. Finally Kirchhof<sup>149</sup> has pointed out certain peculiarities of the activating effect of copper.

#### Antioxygenic Effects

Though it has been difficult to realize, the action of oxygen on rubber should be very energetic under ordinary conditions. Actually, however, the rate of oxidation is almost always slow, and at times it is even inappreciable, in which case there is no technique to detect it accurately. This relative inactivity is not a property of the rubber itself, but is conferred upon it by the impurities, without which deterioration would begin with the tapping of the rubber tree and would proceed rapidly to destruction. Without the non-rubber components, the striking properties of rubber would doubtless have remained unrecognized, and we should still have been ignorant about how to utilize these properties.

These beneficial impurities are soluble in various solvents, such as acetone, and can be removed from the rubber by acetone extraction. After this treatment the tendency of the mass to oxidize increases greatly. Henriques<sup>9</sup> observed this for the first time in 1895, but by mistake he attributed the protective effect to sulfur, a substance practically devoid of action.<sup>137</sup>

The true reason for the stability of raw rubber, *i. e.*, the preservative power of the resinous components of the acetone extract, was perceived in 1912 by Peachey.<sup>22</sup> This natural protection has been confirmed and studied not only by Peachey himself but by Beadle and Stevens,<sup>150</sup> Kerbosch,<sup>151</sup> Whitby and Greenberg,<sup>152</sup> and Bruson, Sebrell, and Vogt<sup>153</sup> (see also references 27, 32, 35, 40, 86, 92, 118, 124, 125, 137).

There has naturally been a desire to know what was the active principle in the resinous extract which gave this beneficial property. Aside from some rather old analyses<sup>150,154,155,156</sup> (see also Dinsmore<sup>157</sup>), there was little data before the works of Whitby, Dolid, and Yorston<sup>158</sup> and especially of Bruson, Sebrell, and Vogt;<sup>153</sup> these last investigators succeeded in isolating two definite substances which were powerfully antioxygenic; *viz.*,  $C_{27}H_{42}O_3$  and  $C_{20}H_{30}O$ .

Of great theoretical interest, these studies are, however, no longer of more than retrospective interest from a practical point of view, for in order to protect rubber against oxygen there is at one's disposal at the present time a complete assortment of artificial substances.

Without doubt, the non-rubber components do not deserve to be disregarded. They assure the almost perfect preservation of the raw rubber, and moreover they often have a fundamental influence on mastication, vulcanization, and lastly on the qualities of manufactured products. In connection with vulcanization, a historical review and some original experiments have been published by Sebrell and Vogt,<sup>155</sup> while other works have appeared since. Somewhat resembling the "bouquet" of wines, the non-rubber components determine the properties of commercial types of rubber and govern the price of the most valuable ones for, like wine, rubber has its "crus" which are in high favor.

Nevertheless from this time on, the antioxygenic portion of the rubber will play an insignificant part for, as forecast by L. E. Weber<sup>83</sup> in 1926, the future depends upon artificial antioxygens. In reality the use of substances to protect against oxidation may be traced back many years. More or less intentionally they have always been used. Among other methods, does not smoking, the origin of which is lost in the mystery of the Brazilian forest, serve to introduce powerful antioxygens, which is what the empyreumatic phenols are?

Organic accelerators have given a new and somewhat unsuspected impetus to artificial protection, for it has been a happy surprise to find that these substances, so valuable in other ways, often retard deterioration. (Schidrowitz and Burnand<sup>160</sup> in 1921, Gottlob and Hofmann<sup>161</sup> in 1925, and also references 63, 70, 83, 91, 100, 118, 124, 125, 137.) This effect is due in part to the shortening of the time of heating and to the lowering of the temperature during vulcanization, but also in part to the specific properties of the accelerators.<sup>137</sup> Nevertheless the true practical safeguard is to be found today in the deliberate addition of appropriate substances, *i. e.*, antioxygens.

The problem of the relation of antioxygens to rubber has been developed so much in the last few years, has brought forth so many works, and has raised so many problems of all kinds that in the present work it would occupy a disproportionate amount of space. It is preferable to consider it later separately. On this point there is now available an interesting publication by Naunton.<sup>162</sup>

However, before going on to another subject it is worth while to review briefly the mode of action of antioxygens, which is still too often badly understood, thereby making their rational utilization uncertain at times.

As was proved in 1921 and later by Moureu and Dufraisse,<sup>163,164,165,166</sup> antioxygens protect autooxidizable substances, among which is rubber, not by making the oxygen surrounding them rarified, or by absorbing the oxygen, but rather by a catalytic action, which slows up the reaction.

In an interesting work Fickendey<sup>21</sup> suggested protecting rubber by adding substances to it which take up oxygen more rapidly than it does, *i. e.*, reducing agents, such as tannin. He obtained the stabilization he expected, but by a mechanism which was exactly the opposite of what he supposed. It is easy to understand this merely by measuring the consumption of oxygen in a simple way; the consumption would increase if the protective form of the reducing agents depended upon their more rapid rate of oxidation and, in a closed vessel, after having added one of these substances there would be an acceleration of the total oxygen absorbed. However, the experiments of Moureu and Dufraisse indicate exactly the opposite; the addition of the protective substance to any autooxidizable substance whatsoever has the effect of lowering the net rate of the combination of oxygen. In other words, when there is a protective action, the protective agent is not oxidized more than the substance which is protected, *i. e.*, both remain unaltered simultaneously.

This has been proved clearly so many times, with so many substances under such varied conditions, and moreover it has been checked by so many investigators

everywhere, that there should no longer be any reasonable doubt about it.<sup>164,165, 166,167;163,168,120,169,137</sup>

Antioxygens do not therefore have a mass chemical action, but are negative catalysts. In their presence oxidation proceeds at a slackened rate, and they are antagonistic to oxygen (as their name implies) so that in some way they render it inactive, without removing it or combining with it.

The practical significance of this idea is easily understood, because from it has come the artificial protection of the present day. This has already been mentioned many times, in particular by Bierer and Davis who, in a meeting at London in 1927, explained how the industrial application of this protection of rubber in industry had its origin in investigations carried out on antioxygens at the Collège de France.<sup>244</sup> Previous to this time, there was a feeling of helplessness against atmospheric oxygen, because it was considered necessary to absorb this gas in order to obtain protection. And as for the absorbing substance itself, what a large quantity would be necessary in rubber to free the air with which it came in contact from oxygen for only a few months. What a contrast with antioxygenic catalysis, which requires so little material to preserve the rubber against almost unlimited quantities of oxygen.

It is moreover possible for each one to make the test for himself, without special apparatus or equipment. It is sufficient to reproduce the experiment by which



**Figure 3—Protection by Partial Immersion (to *ab*) in a Dilute Solution of an Antioxygen (Hydroquinone)**

Photograph of actual size of sample at 5 per cent elongation and after natural aging for two years in a closed space.

Moureu and Dufraisse<sup>163</sup> in 1921 originally recognized that rubber is receptive to antioxygens, like other autooxidizable substances. This test consists in diffusing, by coating or immersion, the surface of the object with a dilute solution of the particular antioxygen (ethereal solutions of hydroquinone often serve the purpose very nicely). The small amount of catalyst which penetrates in this way by diffusion is sufficient to protect in a way that is sometimes astonishing. This experiment can be demonstrated in a more striking way by protecting only a part of the rubber. For example, a thin sheet is immersed in the liquid as far as a mark (*ab* in Fig. 3) and it is exposed to natural or accelerated aging, great care being taken to avoid letting the untreated portion come in contact with the antioxygen. This is the only delicate part of the experiment, because any contamination will be manifest later at the same place by a "protective mark." As long as the catalyst tested has any activity, slight stretching will reveal on the two sides of the line of demarcation *ab* two zones of aging (Fig. 3), which are distinctly different in their aging effects.

In spite of its simplicity or perhaps because of it, this method has lost nothing of its practicability. It is the basis of a method for the preservation of rubber products,<sup>168,169</sup> and it is equally applicable to systematic investigations.<sup>137</sup>



## Part II. The Modes of Action of Oxygen

### 1. OXIDATION PRODUCTS

In organic chemistry, oxidation by free oxygen or autooxidation is rarely a simple reaction, and aside from some special cases, like the transformation of certain aldehydes to the corresponding acids, some leuco derivatives to dyes, etc., it frequently leads to complicated mixtures, from which it is difficult to separate definite products in good yields. This is extremely unfortunate, because many substances are increased in value by oxidation. This would, for example, be true of hydrocarbons, but efforts which have been made to oxidize petroleum products, which are such cheap raw materials, with atmospheric oxygen which costs nothing, have led to no success. Some recent publications have, however, described some regular oxidations of the first members of hydrocarbons, like ethylene and propylene.<sup>206</sup> Likewise fatty acids capable of forming soaps have been obtained from petroleum products but in this case it does not seem as if there would be any dangerous competition with soaps manufactured from fats.

Oxidation of the rubber hydrocarbon is evidently not to be accomplished all at once, because for a long time its unusual properties have assured for it "noble" uses without any one concerning himself with the problem of transforming it into something more valuable. However with its abundance and present prices, the point of view has changed. The characteristic chain formation of carbon atoms in the molecule suggests a cleavage reaction leading to terpene derivatives, a group of substances having a large and profitable market. If one were successful, such a cleavage of the rubber molecule, would certainly have practical applications. Atmospheric oxygen is one of the reagents to be considered for this purpose.

The hope of discovering an advantageous chemical rearrangement of the rubber hydrocarbon increases then the interest, already very great, in obtaining a knowledge of the reaction of autooxidation, because of its close relations with aging. Unfortunately there is very little precise information on the subject. Obeying the same law as its humble allied substances in the mineral kingdom, the rubber hydrocarbon enters into a complex reaction in its combination with atmospheric oxygen.

There is no doubt that a long line of chemists from Hofmann (with gutta-percha) and Spiller (with rubber), including Peachey and his collaborators<sup>1,2,11, 13, 22, 35, 58, 61, 66, 138</sup> have shown great ability in throwing light upon this problem of oxidation. Their efforts, so fertile with useful information, have failed to obtain any definite chemical compound because the amorphous substances which had or had not received even the simplest purification by solution, precipitation, or washing, cannot be considered definite compounds. The formulas given to these substances merely represent analytical data; they do not even pretend to show the chemical nature of the substances.

#### Levulinic Aldehyde and the Pyrrole Test

Perhaps it will be necessary to make an exception in the case of levulinic aldehyde, although there remains much to be done before it becomes certain that this substance is formed normally.

Gorter<sup>23</sup> seems to have been the first to point out in 1912 the presence of an aldehyde in oxidized rubber. Later<sup>22</sup> having obtained the pyrrole reaction after heating with ammonium acetate, he concluded that levulinic aldehyde was present.

With the exception of an experiment on pyridazine by Whitby,<sup>57</sup> this substance has only been detected by the pyrrole reaction.<sup>35, 53, 55, 59, 64, 74, 89, 126</sup> This re-

action, it may be noted, is not of a specific nature, if for no other reason than that it is common to  $\gamma$ -dicarbonyl substances in general. Moreover, under the somewhat crude operating conditions, it appears that its formation in some less classic way is not to be overlooked.

It is accordingly more correct, to speak as some authors do, of a positive pyrrole reaction, rather than to assert positively the still hypothetical presence of levulinic aldehyde.<sup>138</sup> Whatever it shows, this pyrrole test is perhaps worthy of more attention than it usually receives. It may have a certain relation to the degree of vulcanization,<sup>89</sup> and further<sup>126</sup> it may be an early indication of oxidation, although without any simple relation to it.

### Partial Combustion

After having mentioned levulinic aldehyde, traces of formic acid,<sup>55,138</sup> formaldehyde and combustible gas,<sup>138</sup> it might seem useless to call attention to carbon dioxide and water;<sup>27,35,120,138</sup> however, these last waste products ought to be considered briefly. Whether or not they are negligible in the first phase of oxidation,<sup>63,85,120</sup> the quantities liberated increase little by little in the later stages. According to Peachey and Leon<sup>35</sup> in the oxidation of  $C_{10}H_{16}$  by  $2O_2$ ,  $1/4CO_2$  would be formed, *i. e.*, an eighth part of combined oxygen would finally pass to the carbon dioxide state. This has been confirmed in a general way by Kemp, Bishop, and Lasselle,<sup>138</sup> who found even a higher loss of carbon and a loss of hydrogen in the form of water, the total loss corresponding to one methyl group, completely burned, for three to four molecules of isoprene.

The reaction of oxygen with rubber is therefore more complicated than a pure and simple addition of oxygen to the double bonds, since a true partial combustion takes place.

Without any question there is addition, as shown by the increase in weight, to which attention has often been called and which has even been used as an aging test,<sup>3,5,9,10,14,15,23,27,28,30,40,42,74,82,100,118,121,124,135,138,etc.</sup> but the complexity of the phenomena of oxidation reveals the presence of substances which, more than the problematic oxides of rubber, ought to receive the attention of technologists. These substances are the peroxides of autooxidation.

### The Peroxides of Autooxidation

This is not the place to discuss the peroxides of autooxidation in spite of the interest in the subject in connection with the industrial utilization of a substance like rubber. We are going to confine ourselves to a review of a few essential facts.<sup>166</sup>

When it is exposed to free oxygen, an autooxidizable substance unites with one complete molecule by simple addition. The product thus formed has exceptional chemical activity, as manifest in two chief ways: (1) an oxidizing power greatly superior to that of the oxygen from which it was formed, and (2) an energetic catalytic power in certain reactions such as autooxidation itself and especially condensation reactions. Because of their oxidizing properties, these products are called peroxides.

Thus substances deprived of oxygen, and even having reducing power, become powerful oxidizing agents when they are in contact with free oxygen. Although it has been known for a long time from the experiments by Schoenbein and those of Berthelot on oil of turpentine, this fact is too often forgotten in practice, where however it appears constantly and often in a disturbing way. *A fortiori*, the catalytic power, a knowledge of which is of the most recent date, is neglected (see Moureu and Dufraisse<sup>75</sup> and Milas<sup>167</sup>).

Meanwhile what is of more importance to the technologist than a knowledge of this property, whether it is a question of natural products, as will be seen later, or whether it is a question of synthetic products?

Specifically, do not several methods recommended for the polymerization of olefins owe their efficacy fundamentally to the presence of peroxides of autooxidation? In the so-called sodium processes, is not sodium peroxide the active agent, formed by the inevitable surface autooxidation of the metal? In so-called spontaneous processes, or rather with catalysts apparently not peroxidic, is not the active part played by the peroxides of the olefin itself? (In this connection see the work of Conant and Peterson in 1932<sup>177</sup> on the polymerization of isoprene under high pressure.)

Whatever the answer is, peroxides have so often been found in autooxidations that they are to be regarded as necessary intermediates of every oxidation by free oxygen.<sup>75</sup>

There is no reason why rubber should be an exception to the general rule, and it should also be assumed that it too forms peroxides when it is autooxidized. There is, it is true, more difficulty in testing rubber than other substances, the physical state of which makes it possible to penetrate the interior of the mass with the reagents. However, thanks to a correct technique, the presence of peroxides in oxidized rubber, detected for the first time in 1913 by Peachey,<sup>26</sup> has been proved so often since as to no longer leave any doubt of their formation.<sup>27,36,70,76,85,138,146</sup>

The peroxides of autooxidation are too unstable for their chemistry to have become very well known, even in the case of the simplest ones. It is moreover probable that each one has several peroxidic forms, corresponding to different energy levels, and therefore to different chemical activities and to different degrees of stability.<sup>75</sup>

There are still less data on rubber. Without doubt there should be formed besides normal peroxides, aldehydes or other compounds from substances resulting from cleavage oxidations. It is, however, not necessary to know their formulas in order to realize the part played by them, which is well known. One must not overlook the presence of peroxides, *i. e.*, catalysts of condensation, within the rubber, which is unstable from the point of view of its state of condensation.

## 2. THE NATURE OF THE TRANSFORMATIONS

As has just been seen, chemical researches have not furnished much information on the oxidation products of rubber, nor any information on the transformations which are the basis of the phenomena of deterioration. They have, however, contributed one definite fact, namely, that deterioration is a very early effect of oxidation, and only a little oxygen is necessary to accomplish it. This indicates that it is of a catalytic nature.

### Deterioration by Oxidation (a Catalytic Reaction)

The idea that oxygen might act catalytically was expressed in 1913 by Ahrens,<sup>26</sup> but it was Porritt<sup>46</sup> in 1921 who deserves the credit for having recognized it clearly and for having described it plainly. Porritt summarized his idea in these words: "Oxygen is, aside from sulfur, the most important catalyst of rubber from the time of its photo- or biosynthesis until its final utilization in the form of manufactured products." Recent research has only served to confirm this opinion.

In order to recognize that there is catalysis, one may resort to the most common of criteria, which consists in proving that there is a disproportion between the quantity of the reagent and the quantity of the substance transformed. In fact, it requires but little oxygen to cause a deterioration of the rubber.

This fundamental idea is supported by data of twenty years ago,<sup>23,31</sup> but it has only begun to be widely known during the last ten years.<sup>59, 63, 90, 107, 110, 119, 120, 133, 137, 138, 141</sup>

Although the quantity of oxygen theoretically absorbed reaches 47 per cent of the weight of the rubber, the harmful dosage for both raw and vulcanized rubber does not exceed 1 per cent under ordinary conditions. This value of 47 per cent is higher than that which certain authors have given unintentionally. In the autooxidation, free oxygen unites at the double bonds, not by atoms, but by whole molecules, so that it is necessary to assume one molecule of oxygen per double bond for complete saturation. Certain experimental values have reached this high portion;<sup>35</sup> whereas others have been widely different.<sup>61, 138</sup> No conclusions on the true capacity of absorption can be drawn from either the former or the latter, for the first portions of oxygen transform the substance to a profound degree, as has just been seen. The final product which is oxidized is no longer rubber, but products which are formed from the demolition of its chemical structure. The 1 per cent absorption mentioned above also represents too high a maximum value for there is considerable destruction with smaller quantities of oxygen. Furthermore, as part of the peroxides, which are unstable, disappear before they have had time to react, the actual harmful proportion of active oxygen, *i. e.*, in the form of peroxides, must be regarded as very much less than 1 per cent, which is itself a very small percentage.

Systematic researches on the progress of deterioration as a function of the percentage of oxygen absorbed have not yet been made; and they appear to be particularly difficult. However, according to certain indications the harmful proportion would not be a fixed amount, as would be expected *a priori*, but rather would depend upon the conditions and in particular upon the components of the mixture.

Litharge, for example, is one case of a substance which modifies the harmful effect of oxygen. Its favorable influence on vulcanization in hot air is well known and has led to the assumption that it protects rubber against oxygen. Dufraisse and Drisch<sup>143</sup> have shown on the contrary that it is a positive catalyst, and that far from retarding oxidation, it accelerates it. According to this, litharge can exert its well-known useful effects only by its ability to diminish at the same time the harmful effect of oxygen. In fact, a mixture containing litharge is less deteriorated than are other mixtures in the same degree of oxidation. In other words, speaking figuratively, litharge holds the oxygen better. As for the mechanism, it doubtless involves a catalysis which hastens the passage of the harmful but unstable peroxides to final oxidation products which are inactive (Moureu, Dufraisse, and Chauv<sup>172</sup>). It would therefore be misleading to try to find a simple and general relation between the quantities of oxygen absorbed and the corresponding deteriorations.

Finally it is of interest to call attention to the present tendency to assume that the action of sulfur is also of a catalytic nature, simply because it too is active in very small quantities (Bruni<sup>171</sup>). Thus, in spite of apparently being quite different, there should actually be similarities between the modes of action of this highly influential substance and oxygen. Furthermore, in this connection it is a familiar fact that it is possible to vulcanize with oxygen.

#### Oxygen Is the Necessary Agent for Deterioration

Since so little oxygen is necessary for ultimate deterioration, would anything happen if it were not present? In other words, is oxygen indispensable to normal deterioration of the rubber?



The control experiment has been made frequently. Attempts have been made in various ways to deteriorate rubber in receptacles from which the air has been expelled. To confine oneself merely to a simple statement of the old and recent results, one would be rather embarrassed to take sides, for the two opposing points of view have been advanced with equal assurance. Nevertheless, positive evidence leads one to take a stand with all confidence. In view of the importance of the subject, it is worth while to discuss it in detail.

To affirm that oxygen plays no part in the phenomenon evidently means nothing unless it has been possible to avoid this gas when the reaction is carried out. When it is a question of mass oxidation, such as the oxidation of benzoic aldehyde or of sodium sulfite, nothing is easier, than to work practically out of contact of atmospheric oxygen. This is not true in dealing with a catalytic transformation as in the aging of rubber, where the action of oxygen, as was just seen, is not stoichiometric but catalytic. Traces of oxygen, wholly negligible in mass oxidation, would have a considerable effect on the catalysis. It is therefore not improbable that the discordance between the results of the investigators depends upon the difficulty of working in the absence of traces of air.

#### Practical Difficulties of Carrying Out Experiments with Exclusion of Air

Chemists have been warned in recent publications of this difficulty. In view of the fact that experiments are carried out in surrounding air with materials which have been exposed to air for a long time, the need for the greatest care so that air cannot enter during the operation cannot be exaggerated. We have personally become convinced of this fact by an experiment, the object of which was to determine whether or not the polymerization of acrolein to disacryl depends upon traces of oxygen.<sup>173,174</sup> It is very difficult to avoid a proportion of  $1/100,000$  part of oxygen, which we found was sufficient to start the reaction. Such simple operations, to which one does not even give a thought when it is merely a question of a rough protection against the surrounding air, require a separate study of each operation if really complete protection is desired. To obtain a pure gas, to transfer it into a laboratory receptacle, to extract the air adhering to the walls and which is dissolved in the liquids or *a fortiori*, in substances as viscous as rubber, are very painstaking operations which call for a special method of removing the oxygen and do not always assure success. Air impregnates everything, penetrates everywhere, diffuses through joints which are apparently of the best, even against an excess of pressure (unpublished experiments). Rubber tubes and connections are for example not usually suspected, but they must be unsparingly avoided in all precise work, for they permit the diffusion of considerable quantities of oxygen, which Pummerer among others has observed: "According to my opinion these results are profoundly influenced by the fact that it was not possible in the experiments to exclude air completely. Rubber oxides containing from 1.5 to 2 per cent of oxygen are formed by the long passage of the carbon dioxide because of the permeability of the rubber tubing to oxygen. . . ."<sup>243</sup>

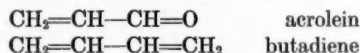
Attention has been repeatedly called in recent years to this danger. Reed<sup>119</sup> found that when he heated rubber, deterioration was almost as bad in commercial nitrogen as in air, whereas heating in carefully purified gas only caused overvulcanization. Staudinger and Schwalbach<sup>175</sup> called attention to the difficulties which they encountered in preparing vinyl acetate sufficiently free of oxygen not to be polymerized by heating in the presence of nitrogen or carbon dioxide. Finally, very recently in 1932 Conant devoted careful studies to this catalytic effect of mere traces of oxygen on the polymerization of butyraldehyde and of isoprene under high pressure. Having stated in an earlier work with Tongberg<sup>176</sup> that oxygen in

the peroxidic form, though an active accelerator, was not necessary to the polymerization. Conant, as a result of new experiments (with Peterson<sup>177</sup>), decided that his earlier point of view was erroneous and explained it by the extraordinary difficulties of avoiding the presence of oxygen. According to this statement, Conant and Peterson have probably not yet succeeded, in spite of their care, in working with isoprene completely free of air. In this way they explain the slight polymerization they have always found.

As for butyraldehyde, with which the experiments are a little less difficult, Conant and Peterson have succeeded in establishing the threshold of activity. They have found this threshold at a molecular concentration of  $5 \times 10^{-6}$  (calculated on the basis of active or peroxidic oxygen), where five molecules of active oxygen begin to exercise a noticeable polymerization on 1,000,000 molecules of butyraldehyde.

Finally, the mixing operation to be discussed later, furnishes a new proof of the difficulty of operating with exclusion of air. (A note by Bary and Fleurent, which has just appeared, calls attention again to the difficulty of avoiding atmospheric oxygen.)

However, even if it were practicable to eliminate all gases, it would not mean that oxygen was then excluded, for there would remain, as traces from the previous contact with air, the non-volatile peroxides of the autooxidation. These cannot be ignored, for they constitute an active form of oxygen. Moureu and Dufraisse<sup>173</sup> have shown this with acrolein, a substance well qualified for comparison with rubber chemically because of its structural similarity with the diene parent compounds of synthetic rubbers, butadiene and its homologs:



A sample of this aldehyde, freshly purified but having been in contact with air is introduced into one of the bulbs of an apparatus formed of two bulbs connected by a narrow tube. The gases are thoroughly driven off by a suitable technique and the system is sealed. One-half the liquid is then distilled into the empty bulb and the two bulbs are separated by fusing with a blow pipe the constriction in the communicating tube. The technique of this experiment involves details which need not be discussed here. Thus the portion distilled under absolute vacuum remains clear, while the residue soon becomes turbid and is slowly transformed into an insoluble polymer, disacryl. Consequently, there must have been in the original liquid a non-gaseous polymerizing agent, left entirely in the residue of the distillation, which must therefore be some substance other than free oxygen. As this agent appeared only upon contact with air it cannot be anything but a peroxide of autooxidation.

It is therefore not sufficient to remove the gas, but it is necessary also to remove the peroxides remaining in the mass. This opinion has since been confirmed several times (Staudinger, Conant, etc.). The justification for this in so far as rubber is concerned is shown in a striking way in experiments by Temple, Cadwell, and Mead,<sup>126</sup> which consist in oxidizing vulcanized rubber in compressed oxygen and stopping the reaction just before the first signs of deterioration. Immediately after this the dissolved gas is removed by a high vacuum. The sample, thus freed from gaseous oxygen, appears identical with the non-oxidized control when the mechanical properties are compared, but it is unlike it in deteriorating incomparably faster than when heated in pure nitrogen. In the words of the authors, rubber which has been oxidized has preserved "potentialities for deterioration." The

peroxides are easily recognized as these potentialities of deterioration which are not removable by a vacuum.

It is relatively easy to free a substance from its peroxides when it is volatile by distillation. However, with substances like rubber which cannot be distilled, there is no method available for removing the peroxides. One has no choice but to destroy them by heating, which is naturally at the cost of a corresponding deterioration, as in the experiments by Temple, Cadwell, and Mead. Consequently, no matter how much care is taken to remove oxygen, rubber will always deteriorate slightly upon heating. This has in fact been observed by several investigators who have heated rubber *in vacuo* or in an inert gas. However, after the first period of heating is over, the substance remains almost unaltered, not as was believed because a state of equilibrium has been reached, but because of a lack of catalysts it can no longer be transformed.

It is needless to say that the temperature and the time required to destroy the peroxides have not been determined, and there is the greatest uncertainty about these factors.

In brief, to work with any substance in the complete absence of detectable traces of free oxygen or peroxidic oxygen proves difficult with simple substances, and is impracticable with rubber in the present state of its chemistry. There is nothing more to be hoped than to rarify the oxygen more or less, the essential point being to remove enough so that its degree of dilution is so great that it is justifiable to disregard the remaining trace.

Thus far the precautions which have been considered sufficient by investigators have often been passed by in silence or only mentioned briefly in published papers. This makes it difficult to form an opinion on previous experiments which tend to show that rubber does deteriorate in the absence of oxygen. For every reason these experiments should be repeated, bearing in mind recent data, and should be described minutely in the smallest details under the penalty of not being accepted otherwise. Today one should no longer be satisfied with the simple statement that the experiment was carried out with exclusion of air.

Meantime, it is reasonable to agree with those, and there are many of them, who have succeeded in obtaining only a slight or negligible deterioration when they have removed the oxygen sufficiently.<sup>5,9,19,21,23,26,31,32,46,63,74,82,93,103,119,120,121,126,130,137</sup> According to these authors, oxygen would be the necessary agent for the chemical deterioration of rubber, at least of the most evident forms of deterioration.

Perhaps when the technique has been perfected, it will be necessary later to make some slight reservations. It might not be impossible, for example, that extreme ultra-violet radiation, after-vulcanization, and still other causes may have effects which are independent of those of oxygen. However these are but subordinate causes of the deterioration of rubber, for the principal one which is the cause of most of the damage is oxygen. Recently there seems to be agreement on this point, or at least for several years disagreeing voices have no longer been heard, so that at the present time the chief cause may be regarded as conclusively established.

### 3. SIGNS OF DETERIORATION

Deterioration is of interest to the manufacturer and consumer only in so far as it affects the mechanical properties of the rubber unfavorably, such as the flexibility and elasticity. The ideal way would be to follow by chemical means the various aspects of deterioration. Unfortunately this is still very far in the future, and if an arbitrary classification is desired one must rely upon changes in appearance. The chief features of this problem will therefore be reviewed.



### Increase in Solubility (the Extracts)

Numerous references<sup>3,9,28,42,49,64,80,109,118,121,124,135,136,178,230,etc.</sup> show that in rubber which is undergoing deterioration there is a noticeable increase in the part which is soluble in solvents, and which continues to be called the extract. The most commonly used solvents for these extractions are first of all acetone, then alcohol, chloroform, water, and alkaline liquids.

As a general rule, the extract content increases with the progress of deterioration, although it has not been possible to establish any simple relations between the two phenomena. The proportion of soluble substance ordinarily passes through a maximum and then diminishes. This maximum does not appear to have much practical significance, since this maximum corresponds to an advanced state of aging because of the extract having changed by oxidation. In a few exceptional cases of deterioration, the greater part of the substance becomes soluble in acetone up to nearly 80 per cent<sup>28</sup> and even 93 per cent.<sup>230</sup>

Neither the nature of the transformation nor the components of the extracts have yet been established.

### The Conversion to Fat, or to a Sticky Condition

This type of deterioration, although it is sometimes reached by the vulcanizate, is especially manifest in raw rubber, where it is accompanied by a considerable lowering of the viscosity of its solutions. In virtue of this peculiarity it can be detected and followed with great precision in its progress, as has been done recently by Fleurent and Bary.<sup>179,180</sup> This phenomenon has also been the object of numerous other works.

This is not the place to review the part played by oxygen, except to mention its extraordinary activity in bringing about a sticky condition and a drop in viscosity.<sup>84,90,110,120,133,141,242</sup> Fry and Porritt<sup>90</sup> for example have observed a lowering of almost one-half the value of the viscosity where the degree of oxidation is only of the order of magnitude of 1:10,000.

On the contrary, it is necessary to discuss the cause of the deterioration because of the term "depolymerization" frequently used to describe it. This term has in chemistry a meaning too well-defined for it to be used in any other sense. It denotes the inverse reaction of that which was formulated at the beginning of this article, *i. e.*, a cleavage of the molecule, with rupture of the carbon chain and the resulting formation of a double bond. Furthermore this cleavage results in a lowering of the molecular weight and an increase in the total energy, brought about by the double bond. In brief, depolymerization is manifest from a practical point of view by a decrease in the molecular weight, by an increase in the "unsaturation" and in the heat of combustion, *i. e.*, variations the measurement of which must naturally have preceded the use of the word "depolymerization."

Unfortunately, this is not what takes place in the case of rubber. As Fisher and Gray<sup>181</sup> remarked in 1926, the term "depolymerization has been used very loosely, apparently without any definite experimental data other than the change in viscosity to substantiate it."

Measurements published at the present time are not in favor of depolymerization, and the molecular state of aggregation does not usually vary during resinification, at least not within the limits of experimental error, limits somewhat large, it is true. When in exceptional cases much greater deviations have been recorded, they are in a sense opposed to depolymerization and indicate condensation. Here it is not a question of the molecular weight, which is too high to be determined even approximately and thus to be of any utility.

It was in this way that Messenger<sup>182</sup> concluded from his thermo-chemical measurements that there is no change within the molecule, that is, there is no depolymerization during the drop in viscosity resulting from mastication or from sunlight.

The problem of unsaturation has more often occupied investigators because of its intrinsic interest in connection with the chemistry of rubber. It is measured by the iodine index as modified in the method of Kemp,<sup>183</sup> which is an adaptation of that by Wijs.<sup>181,183,184,185,186,187,188,226</sup> It is also measured by the bromine index.<sup>188,189,84,186</sup> by the oxygen number (method of Prileschajew with perbenzoic acid,<sup>187</sup>) or even by the rate of the reaction with sulfur.<sup>190</sup> According to Fisher and Gray<sup>181,185</sup> and also Kemp and his collaborators<sup>183,188</sup> the processes (oxidation, heating, mastication, etc.) which involve the so-called depolymerization do not give evidence of any extra chemical capacity. The changes which have been found would lead rather to the opposite conclusion. Unsaturation instead of increasing, as would result from a depolymerization, has rather a tendency to diminish.

It is however inadvisable to draw hasty conclusions against the hypothesis of depolymerization as the authors of these experiments do, because the phenomenon could still be possible within the limits of error of the measurements. For example, if the molecules of a mass of rubber are divided into two equal fragments, then the molecular weight will diminish to one-half its value, while the number of double bonds, equal at the beginning to  $n$  per molecule, will increase in the ratio of  $n$  to  $n + 1$  (1 by cleavage). If  $n$  greatly exceeds the number 100, *i. e.*, 100 molecules of isoprene per original molecule, the technique of the measurement is not sensitive enough to detect the change. Recent data, principally the excellent work of Staudinger, have made chemists familiar with the molecules called "macromolecules," which are much larger than an agglomerate of 100 isoprenes. An extensive depolymerization can then take place which in the present state of precision cannot be detected by measurements.

Thus the idea of depolymerization, if it is not definitely contradicted by direct measurements, no longer offers any proof of its validity. There is left only the uncertain support of a hypothesis relating the viscosity values with those of the molecular size. When it is said that rubber is depolymerized in the course of fluidification, it is assumed that a drop in the viscosity can have no other cause than a decrease in the state of molecular aggregation.

According to Duclaux (private communication which is to be published later, and Blow<sup>193</sup>) nothing necessitates such a positive view, and above all there is nothing to warrant its being considered self-evident. A maximum in the viscosity-molecular weight might not even be improbable. The subject is therefore still within the realm of conjecture, and there it will remain until physical chemists have settled upon a general theory of viscous substances.

Nevertheless, one particular case has already been settled by Staudinger,<sup>191</sup> that of filiform molecules. This investigator has worked out a formula relating the length of the molecule to the coefficient of viscosity, and after he verified it experimentally he used it to obtain, by extrapolation, the values of the molecular weight, calculated by hundred-thousands.

The concept of filiform molecules applied to rubber has proved to be most fruitful. It has made it possible to explain, simply and logically, the sensitivity to traces of oxygen; when a mass is made up of long molecules it requires only a little oxygen to split them all by oxidation. According to this theory, the substance would become fluid by stoichiometric cleavage and not by depolymerization.

This line of reasoning has the advantage of avoiding a serious difficulty, perhaps the most serious difficulty that can be brought against the theory of depolymerization. In this theory, in fact, the active agents can function only catalytically;

and particularly when traces of oxygen react the effect must be a catalytic one. Consequently the stable state of crude rubber must be a depolymerized one, since it is brought about by catalysis. In that case what is to be said of vulcanized rubber, and is this state brought about by catalysis? Should we give up the idea of a more highly polymerized state here in order not to have to assume two catalytic effects which act under comparable conditions on the same system and alter the system in exactly the opposite direction, one a polymerizing effect and the other depolymerization?

In spite of its advantages, every theory which invokes the stoichiometrical reaction of oxygen has, in common with the depolymerization theory, the fault of not taking into account a factor which today can no longer be ignored, *i. e.*, the catalytic polymerizing power of peroxides, the prevalent formation of which, even in rubber, has already been mentioned.

Every autooxidizable substance which has a tendency to polymerize, always does polymerize more or less under the influence of its own peroxides when auto-oxidation has taken place. The word polymerize is used here in the wider sense recently defined by Carothers.<sup>192</sup> Olefinic substances are particularly subject to this reaction on account of the tendency of the double bond to become saturated through condensation, and this is also true of substances with relatively large molecules, such as drying oils and the more simple derivatives of ethylene.

Since peroxides have been found to destroy the ethylenic bond, it is not evident why they spare those of rubber, particularly since the bonds of isoprene are particularly sensitive.<sup>176,179</sup> Would it not then be more satisfactory to try to explain the facts by assuming that peroxides fulfil their normal function? All that is necessary is to make use of current ideas on the structure of rubber.

Rubber is probably not a definite chemical compound, but a mixture. This hypothesis, advanced a long time ago (see Park<sup>196</sup> and Acken, Singer, and Davey<sup>211</sup>), has become more important in recent years, thanks to the work of Duclaux,<sup>194</sup> Pummerer,<sup>195,206</sup>, etc. Park,<sup>196</sup> Feuchter,<sup>197</sup>, etc. Hauser,<sup>198,200,201,202,203,204</sup>, etc. Dinsmore,<sup>199</sup> Staudinger,<sup>205,141</sup>, etc. Whitby,<sup>207,208</sup> Fikentscher and Mark,<sup>209</sup> Midgley<sup>210</sup> Davey,<sup>211</sup> Freundlich, Bary, Mark, Auer, etc. Rubber would then be made up of two or more associated phases. However in all probability, the complexity does not stop here; mechanical properties certainly do not depend upon a chaotic arrangement of the different phases, otherwise efforts to reproduce these mechanical properties in synthetic materials would have been successful long ago. Everything points to the belief that the peculiar characteristics of rubber are determined by the way in which its constituents are arranged; in this case rubber would not only be a composite substance, but one highly organized. Hauser,<sup>203</sup> Fikentscher and Mark<sup>209</sup> have already suggested a spiral winding.

If one of the essential components is polymerized under the influence of its peroxides, it will be changed to the extent of becoming unable to play its original role in the general equilibrium. With a view to making these ideas definite, let us take for example, the solid, elastic network which has been suggested by several authors to explain the nerve of rubber, and let us suppose that its component is very sensitive to the resinifying attack. It becomes more and more friable, and becoming dispersed or perhaps agglomerated into a flocculent state, it gradually disappears in so far as offering any structural resistance is concerned. Consequently the mass, left to the mercy of the forces of cohesion of its liquid components alone, liquefies little by little.

If this mechanism or some similar one is adopted, not only is there no longer any need of assuming that the substance is depolymerized, but on the contrary it points to a resinifying polymerization. This is in keeping with the ordinary ef-

fects of oxygen, the dominant influence of which on the conversion to fat is explained in this way very simply and in all its aspects.

Furthermore this mechanism conforms to the mechanism of gels, which also become fluid, not by a process of disaggregation of the mass, but by a destruction of the solid structural framework (solution, flocculation, or crystallization). To mention only a single type, this is the case with gels of sodium chloride and hydrocarbons, where there should be no doubt about the mechanism of fluidification.

To return to rubber, this hypothesis is in conformity with an observation by Blow<sup>193</sup> on the subject on the effects of milling. Furthermore it finds support in experiments by Hauser and Hünemörder<sup>215</sup> and those of Grenquist,<sup>130</sup> who have seen the original globular structure disappear and fuse in the middle as deterioration progresses. According to Grenquist, the variations in the plasticity are more or less reversible as long as the globular structure has not been destroyed by oxygen. Finally the agreement with an observation by Klein and Stamberger<sup>212</sup> should be mentioned. A substance which in the beginning shows homogeneous solutions in the ultra-microscope, becomes distinctly heterogeneous when it has been highly degraded by milling. Are not the granules which appear the result of a flocculation of the resin into which the elements of the solid network have been converted?

Whatever is the system which will be accepted in the future, it would be preferable to abandon the word depolymerization for indicating the loss in viscosity of the rubber, and to substitute for it the word "degradation," which is already very much used, which is just as explicit and which does not have the disadvantage of involving a somewhat doubtful hypothesis.

### Hardening

The theoretical difficulties which confront one in trying to interpret the conversion to fat are of no concern in the problem of hardening. There is no hesitancy in attributing hardness to the peroxides which, behaving in a normal way, resinify the substance.

No more is known about the chemical nature of hardening than is known about the other effects. Are there several kinds of hardening? This is not known. However it appears as if light produces a hard oxidized film on the surface, which cracks each time the rubber is stretched. Williams<sup>82</sup> seems to have been the first to observe this fact, and to distinguish it from the other kind of hardening which is deep-seated. Later this film would exercise a certain protection, at least against light.

### Crazing or Surface-Cracking

Crazing and cracking have been studied chiefly by Williams<sup>82</sup> and by van Rossem and Talen<sup>139</sup> but also under different subjects by numerous others.<sup>5,77,82,87,91,93,101,102,104,122,127,128,129,134,139,216</sup> In order for them to form, there must be slight stretching and at the same time an attack by oxygen.

Thomson<sup>5</sup> as early as 1885 observed that stretching made rubber more vulnerable to ozone. The truth of this observation was verified in 1925 by Haushalter<sup>216</sup> and numerous times since (in most of the references just given).

It is a curious and unexplained fact that the sensitivity to cracking passes through a maximum a little above the zero point of stretching; this is called the critical elongation and corresponds to the maximum sensitivity. According to Haushalter, Jones, and Schade<sup>102</sup> (see also Kearsley<sup>127</sup>) the maximum would be better defined by the same ratio on a basis of the stress rather than on a basis of the elongation.

It is unfortunate that under service conditions the dangerous elongation is very low, i. e., only of the order of 10 to 20 per cent.<sup>77,82,101,102,122,127,128,129,134,139</sup> Now



with a substance as extensible as rubber, there are few of its products which when at rest are not under this elongation in some of their parts.

The second indispensable factor, the attack by oxygen, is still not well understood. It does not seem as if free oxygen is the contributing factor, at least directly, for cracking does not take place in a Geer oven, even under stress, nor in the Bierer-Davis bomb.<sup>122,128,129</sup> On the contrary sunlight is very effective, in fact to such an extent that it appears to be indispensable, and from this has arisen the term "sun-cracking" sometimes used. In reality, sunlight is not directly responsible for this, as Williams<sup>82</sup> and later van Rossem and Talen<sup>139</sup> have proved. Williams has shown that a sheet exposed to sunlight changes almost as soon on the shady side as upon that which is directly exposed. Van Rossem and Talen have obtained the same effects by exposing their samples outdoors only in the night time, and they have with very good reason proposed the term "atmospheric cracks" to designate this kind of damage. Sunlight does not therefore act directly. According to the last two authors it might even have on the contrary a favorable effect by forming the protective oxidized layer which has just been mentioned. What is then the active agent? At the present time the feeling is that ozone is the guilty substance. As has been known for a long time, ozone attacks rubber energetically, and the use to which Harris put this fact is also well known. Within the last few years it has been found out that dilute ozone reproduces the characteristics of atmospheric cracking,<sup>122,127,128,129,139</sup> and van Rossem and Talen also believe that ozone is the sole responsible agent. Thus the problem of the normal presence of ozone in the air arises.

It is known that at a great height in the stratosphere there exists a layer of ozone, the importance of which Fabry and Buisson<sup>217</sup> have established by their notable spectrophotometric researches, and the results of which have since been confirmed by Dobson and his collaborators.<sup>219</sup> In the lower atmosphere chemists believe they have identified ozone and have even determined the quantity, but their experiments are not conclusive because they have determined nothing more than an oxidizing power which is common to all types of peroxidic substances, and these are to be found, as will be seen, on the surface of the earth. These discoveries would therefore have been questionable had not Fabry and Buisson<sup>218</sup> by their spectrophotometric method, applied to a thick bed of surrounding air, succeeded in proving the actual existence of traces of ozone in the lower atmosphere.

Nevertheless the undeniable fact that ozone is normally present in the atmosphere is not sufficient to explain all the phenomena of cracking. It is difficult to see where, among other things, a bright atmosphere favors the development of cracks. By what mechanism does light play a part? Since its action is not direct, what kind of an indirect effect does it bring about? With its active waves removed by filtering through the highest strata of the atmosphere, would it still be capable, as some believe, of forming ozone near the surface of the earth? This is improbable. Moreover, according to McKee and Depew,<sup>104</sup> light with little actinic radiation favors cracking. In that case would it be necessary to assume, as do van Rossem and Talen, that we are supplied with ozone at the expense of the stratosphere by atmospheric currents?

In the face of these difficulties, would it not be preferable, without denying in any way the part played by ozone, to consider another agent? A curious comparison presents itself. Rubber cracks under conditions similar to those when a photographic plate receives an impression in darkness. It is known in fact that when irradiated the most unexpected substances acquire the well-known property of giving off a material emanation capable of making an impression on a sensitive film. This phenomenon, which was discovered for the first time in the middle



of the last century by Moser in 1842 and by Niepce de Saint-Victor in 1857 and 1859 (see the history by Keenan<sup>220</sup>), has been studied by Russell<sup>221</sup> and later by numerous other authors. It has been shown that it is brought about by peroxides, including hydrogen peroxide, which are liberated slowly by the substances previously autooxidized by light. The latent image produced on the photographic plate is also a very sensitive test for volatile peroxides;<sup>220</sup> among the latter hydrogen peroxide gives the same sort of impression on a sensitive film as does light.<sup>222</sup> The oxidizing emission, which must evidently begin below the luminous range, sometimes continues in darkness for long periods, *i. e.*, for days and even weeks.

This is a very general property, and it would be tiresome to enumerate all the substances in which it is found. In short, every organic substance possesses this property, particularly plant substances and the many substances of plant origin, rubber among others (see van Rossem and Dekker<sup>76</sup> and Busse<sup>146</sup>). As every unprotected surface soon becomes covered with organic dust, if not even with plant life, it follows that every surface exposed to unfavorable influences must emit oxidizing vapors both by night and by day. This ought to be the case especially with the walls and the roofs of our dwellings. Why would not the oxidizing emanation which is capable of attacking the silver salts of a photographic plate be the agent which also attacks rubber? This would explain better than does ozone the chief peculiarities in the formation of cracks. This would also show in a better way why sunlight, because it accelerates autooxidation, which in turn forms peroxides, would favor cracking without being the direct cause of it (Williams,<sup>82</sup> van Rossem and Talen<sup>139</sup>). This would also explain how an illumination, which is only slightly actinic and incapable of forming ozone, would suffice for the formation of cracking for the reason that it would be capable of bringing about autooxidation. Finally it will be understood how in order to have cracking occur at night rubber must be put outdoors (van Rossem and Talen, *loc. cit.*), *i. e.*, exposed to surface emanations, which are oxidized themselves during the day when there is the maximum solar energy.

It is conceivable that antioxygens (which are not antioxidants) have no protective effect against ozone or peroxides, or against whatever the oxidizing agent responsible for atmospheric cracking. This has in fact been established. Some antioxygens have a slight and uncertain protective action, such as paraffin, which extrudes to the surface and forms a coating which is not readily attacked.

#### 4. FACTORS WHICH INFLUENCE THE RATE OF OXIDATION

Nothing is of greater benefit to the manufacturer, middleman, and consumer of rubber products than to know the factors which influence the rate of oxidation of the products. Mention has been made above of the retarding effect of antioxygens, so now the question is only of the influences which promote oxidation.

##### Autocatalysis (the Period of Induction)

The autooxidation of raw rubber follows an autocatalytic course. The rate, at first inappreciable, then very slow, increases gradually during a more or less prolonged initial phase which is known as the "period of induction." Following this, the rate increases rather abruptly to a definite point, and finally diminishes when a greater part of the substance is oxidized.

The phenomenon has been described by Ostwald<sup>24</sup> with the aid of curves published by Peachey, which have the characteristic S-form. This has also been described many times since, though in the case of vulcanized rubber the diagrams are not very successful in showing the phenomenon.<sup>137</sup>

In order to explain the symptomatic stage, *i. e.*, the period of induction, attention has been directed for a long time to the accompanying conversion to fat, or rather, as was once thought, the depolymerization. Rubber it was thought reacts at first only slowly with oxygen, because in the beginning it is not in a very receptive state. In order to become receptive it must become depolymerized, that is, more reactive. In other words, the appearance was confused with the true facts, or the cause with the effect. Autooxidation governs stickiness, but in no way depends upon it. It progresses according to its own laws almost independent of the state of the mass, if this is not in a condition where the action of the oxygen is interfered with. At all events it does not owe its increase in rate up to the end of the period of induction to the so-called depolymerized state; for vulcanized rubber does not pass through this state and yet it oxidizes more rapidly than raw rubber.

Furthermore a glance at the chemical facts cited in the previous section would fail to show why the activity is higher not only toward oxygen but toward all other chemical reagents.

After all, this type of autooxidation is not an isolated phenomenon, but on the contrary is a rather commonplace property, common in fact to a host of substances. To mention merely one case, limonene possesses this property, as can be seen from its diagram of oxidation given in the beginning of this article (Fig. 2). The curvature at the beginning is characteristic of autocatalysis. Now, during the initial phase this terpene undergoes no change which resembles in any way a conversion to fat; it does not become fluid, nor does it depolymerize. In this particular case, as in many others, it seems impossible to attribute the period of induction to a change in the state of physical and chemical aggregation. Why should it be otherwise in the case of rubber? It is therefore more reasonable not to try to interpret this in any unusual way, but to place rubber in the ordinary category of autooxidizable substances.

Two principal hypotheses have been advanced to explain this tendency of many oxidation reactions to be retarded. According to the first hypothesis, peroxides are positive catalysts; they accumulate in proportion to the oxygen which reacts and the rate increases. This is autocatalysis in the strict sense of the term.

According to the other hypothesis, autooxidizable substances, even those which appear to be pure, contain negative catalysts of an unknown nature. The peroxides formed in the beginning would gradually first destroy these antioxidants, and would progressively increase the rate to its normal value. As a matter of fact, the diagram of autocatalysis is obtained when a little antioxidant is added to a substance which undergoes simple oxidation.

It would be rather premature to choose between the two theories, which are both supported by sound arguments.

#### Physical Agents

There is hardly any need of speaking of the acceleration produced by heat, which is known to every one. The same thing is also true of light, which has received the attention of many investigators.<sup>4,16,17,18,19,23,27,41,46,49,51,60,66,77,80,82,87,88,89,93,94,104,107,122,125,128,129,130,136,213,223,224, etc.</sup>

The most active radiations are those with the greatest frequency, and when the ultra-violet region is reached the rate increases rapidly. It seems, however, that red rays and even infra-red rays are still accelerators, though much less energetic ones.

#### Methods of Treatment—Operating Methods

Two operations of mastication and vulcanization, which are unfortunately essential to manufacture, predispose rubber to attack by oxygen.

The influence of mastication must according to Thomson already have been noted by Miller, and it has been reported several times since.<sup>213, 36, 92, 120</sup>

The influence of vulcanization might well lend itself to discussion because there is some disagreement among various investigators, a disagreement which doubtless arises from the differences in technique used. Some think that vulcanized rubber oxidizes less rapidly than does raw rubber.<sup>19, 26, 35</sup> It must be admitted that the most numerous, the most precise, and the most recent works give rather the opposite impression, which Martin expressed when he said<sup>86</sup> that the most stable state of rubber toward oxidation is the raw state, and the more advanced the state of vulcanization the greater is the sensitivity to oxygen.<sup>9, 38, 39, 40, 43, 44, 47, 63, 83, 86, 94, 118, 120, 125, 137</sup> On the other hand, the opinion has been offered<sup>42, 52, 83</sup> that under-vulcanization favors the tendency to oxidize. Others<sup>93</sup> think that under-vulcanization affects rubber in a different way according to the ingredients which it contains.

### Foreign Substances

Certain foreign substances have so great a deleterious influence that great care should be taken to avoid them either in the rubber itself or in the components of the mixture.

*Moisture.*—From the point of view of the addition of oxygen, the effects of water are not definitely known. Certain authors consider that moisture plays no part,<sup>35, 93</sup> others that it may have at times a harmful action,<sup>104</sup> and finally several authors believe that it is a protective agent.<sup>214, 21, 43, 64, 83, 125</sup>

*Free Sulfur.*—This substance has no appreciable influence.<sup>137</sup>

*Metallic Salts.*—In contrast to sulfur, metallic salts are among the most active catalysts of oxidation, and from this point of view some of them are dangerous, especially manganese compounds<sup>7, 48, 50, 53, 54, 55, 83, 89, 98, 99, 116, 140, 233</sup> and those of copper.<sup>3, 4, 6, 7, 12, 21, 36, 48, 51, 53, 55, 60, 76, 83, 89, 91, 98, 99, 105, 116, 132, 140, 224, 225, 227, 228, 229, 230, 231, 232, 233, 241</sup> The deleterious effect of manganese and copper is such that the slightest traces should be avoided. Bruni and Pelizzola<sup>50</sup> advanced the idea that the natural tendency of rubber to oxidize depends upon the manganese originally present. Spontaneous fires caused by the presence of copper in rubber have been reported.<sup>105</sup> It has also been urged that the plantations give up their copper treatment (fungicides and insecticides) with Bordeaux solution. Finally, every one knows the remarkable works of C. O. Weber on the rapid destruction of rubberized fabric as a result of traces of copper contained in the dyes in the fibers.

Without being so dangerous, other metals are also capable of accelerating oxidation, *e. g.*, iron,<sup>7, 21, 224, 225, 241, 60, 76, 89, 98, 99, 121, 140</sup> lead,<sup>143</sup> mercury,<sup>99, etc.</sup> Other substances have been reported as deleterious, such as oxidizable oils. They merit special study.

## Part III. Oxidation from the Technical Standpoint

There was a time when the rubber technologist did not consider that the oxidation of rubber was of any direct concern to him, but that it was logically a problem for the suppliers of the rubber and for the consumer of his products. This is no longer true, and the problem of oxidation is becoming more important each day in the rubber factory, as already evidenced by the attention given to it in mixing and in aging tests.

### 1. TESTS OF THE STABILITY OF RUBBER

Even when the source of rubber, its chemical composition, the properties of its compounding ingredients and the various processes which rubber mixtures undergo are all known, the rubber manufacturer may still be uncertain about the quality of the products which he sells, and particularly about their aging properties. Accordingly efforts have been made for a long time to find a means whereby the behavior of a rubber product upon aging can be foreseen. It is here that stability tests play their part.

These tests involve two distinct phases: first, the problem of accelerating deterioration and at the same time simulating long, natural aging, *i. e.*, the problem of artificial aging, and, secondly, the problem of how to judge the deterioration brought about by an artificial test.

#### Artificial Aging

Rubber may be aged by subjecting it to light, to heat (the Geer oven), or to compressed oxygen (the Bierer-Davis bomb).

Since light and heat act in conjunction with air, artificial aging by any one of the three processes mentioned above is an "oxido-aging."

The Bierer-Davis bomb, rightly esteemed by technologists, calls for certain precautions, for it accelerates oxidation so much that there is at times a danger of completely altering the course of the deterioration from that of the slower natural aging. Bierer and Davis have warned against this more than once themselves,<sup>67, 91</sup> as have Williams and Neal.<sup>132</sup>

Aging is in reality the resultant of successive reactions which depend upon autooxidation. When the relations among these several reactions are changed by exaggerating some of them disproportionately, there is a discordance between the final result and natural aging.

This is not difficult to realize, for if natural aging is a result chiefly of catalysis by peroxides, it is obviously necessary to allow these peroxides the time to fulfil their function, otherwise the system will undergo such extensive oxidation that it will not be a duplication of natural aging.

Thus when acrolein is oxidized there is an abundant formation of disacryl by polymerization, but when on the contrary it absorbs oxygen too rapidly it no longer polymerizes, because the molecules oxidize instead.<sup>173</sup> A false idea of the natural aging of acrolein will thus be obtained if it is allowed to absorb oxygen too rapidly.

The same facts are doubtless true, *mutatis mutandis*, of rubber. The experiments of Temple, Cadwell, and Mead<sup>126</sup> indicate in fact that the two phases of oxido-aging, the absorption of oxygen and the subsequent deterioration, are unequally accelerated in the Bierer-Davis bomb when cold, the first phase being accelerated disproportionately more than the second phase. Likewise the pyrrole test is far more intense with the bomb than with the Geer oven.<sup>126</sup>

It may therefore be often better to prolong somewhat the time of the test rather than to surfeit the rubber too quickly with oxygen, particularly since so little oxygen is required to bring about an advanced state of deterioration.

Similar remarks apply equally well to light tests and to heat tests. Except under unusual conditions where the service warrants it, it is useless and probably harmful to make a test too severe, *i. e.*, to submit the rubber to too high temperatures or to radiation of too high frequency. Booth, for example,<sup>147</sup> has recommended for certain air bags tests in compressed air at a high temperature (120° C.). The results will then be difficult to interpret in terms of stability under service conditions, which are after all the only conditions which are of any concern to the manu-

facturer and to the consumer. Weightman<sup>97</sup> and Yamazaki<sup>96</sup> have in turn laid stress upon the errors which arise from the careless use of too active radiation in aging tests.

The ideal situation would without doubt be to have a rubber resistant simultaneously to all influences tending to deteriorate it. Since this is still a long way off, it is better to limit the objective in a more modest way to improving the resistance of a particular product to the influences which are most closely related to those in natural aging.

Both the manufacturer and the consumer would give a great deal to be able to foresee even approximately the span of life of a product. Moreover, there have been frequent discussions about the relations among various methods of aging, and there have been many attempts to assign coefficients to the tests with a view to expressing their equivalence to the time of natural aging.

These problems have been discussed at several meetings and in numerous publications. No general rule has yet resulted from these controversies, except that there are great differences among the experimental results, depending upon the type of test and the conditions.

Accordingly one is forced to give up, at least for the present time, the idea of foretelling the span of life of a product from its behavior in artificial aging, particularly since the conditions of natural aging are ill-defined and unforeseeable. The temperature and ordinary illumination, for example, vary in a way which defies calculation, even in the most approximate way.

However, with these restrictions, artificial aging tests are of great interest, and they have become indispensable to regular factory operation. They are of indisputable value for comparing given types of products under similar conditions, and they make it possible to control each ingredient and each process. Finally they assure the consumer a highly uniform product in successive purchases.

It would doubtless be desirable to carry on further investigations on the problem of aging tests, with a view particularly to making it no longer necessary to work in the dark in choosing the proper deteriorating influences and their intensity. To accomplish this, it will first of all be necessary to obtain a better insight into the innermost mechanism of deterioration, a study which appears to be purely theoretical, but the great practical utility of which is manifest.

### Tests of Deterioration

It is not sufficient merely to accelerate aging, for it is still necessary to be in a position to measure the extent of the damage. Tests of the deterioration which fulfil this latter requirement represent then at least one-half of the value of stability tests. Deterioration tests may be classified in three chief groups, according to whether they are based on changes in appearance, changes in physical properties, or chemical changes.

The way to estimate the progress of deterioration by surface changes is to observe such effects as tackiness, hardening, cracking, and a lowered resistance to tearing. Though easy and reliable, this method is unfortunately neither sensitive nor precise, and it cannot be expressed quantitatively. Moreover, measurements of the mechanical properties are generally favored, particularly the tensile strength and elongation at rupture. Other methods are of interest in that they do not destroy nor even affect the samples, and consequently make it possible to carry out successive measurements on the very same test-piece. The torsion oscillation test recommended by Villey<sup>236</sup> belongs to this class of tests.

Mechanical tests are useful not only because they give quantitative results,



but also because they represent properties actually utilized. They are accordingly the best kind of tests to carry out on purchases of rubber goods.

On the contrary, as already mentioned by Kohman,<sup>120</sup> they are in some ways inconvenient for systematic investigations. First of all, they are not always easy to carry out, as for example, with sponge rubber, where Stevens has recourse to an ingenious though complicated artifice.<sup>108</sup> Moreover, in the case of oxidizing, they give only indirect indications of the effect of the oxygen, which results in erroneous conclusions. Mechanical tests depend, moreover, upon another factor besides oxidation, namely, the state of vulcanization. Finally they give the first indications of a change only after an advanced state of the attack by oxygen, and in view of the complexity of the phenomena, it is possible to obtain only a vague idea of the actual course of the oxidation distinct from its numerous effects.

It would be necessary, or at least it might be advisable, to resort from time to time to chemical tests, without however giving up the mechanical tests, which always ought to be the ultimate criterion. As a matter of fact, this procedure has been followed at various times; the total increase in weight, the increase in the weight of the extracts, the pyrrole test, and what is the most certain test, the rate at which oxygen is absorbed, have all been determined (see references already given). The oxygen-absorption method<sup>22, 32, 35, 59, 63, 82, 92, 120, 137</sup> has been used both with the technique of Peachey<sup>22</sup> and that used by Moureu and Dufraisse<sup>137</sup> in their general investigations of autooxidation, but it has not yet been developed to the point which it deserves. There is every reason to believe that, with the patient and studious use of all these methods, it will be possible to explain step by step, to the great advantage of the rubber industry, the complicated part played by oxygen in the transformations of rubber.

## 2. MASTICATION

Since oxygen has so deleterious an action, it would seem as if all efforts should be directed toward avoiding its bad effects. In reality, it has recently been discovered that it is an indispensable agent in one of the essential treatments which rubber undergoes, that is, mastication, so it is no longer a question of avoiding oxygen at any cost, but of being obliged to allow it to assist in the process.

The principal object of mastication is to convert raw rubber, which is resistant to such treatment, into a plastic mass capable of being worked in various ways and particularly of being calendered. At the same time, the milling process serves to incorporate the necessary ingredients.

### Plasticization by Milling Is a Result of Oxidation

Since the time when, about a century ago, Hancock conceived the idea of plasticization, it has been the subject of many observations. According to some, it does nothing more than change the mass mechanically, as in crushing a jelly, whereas others consider it to be a physical phenomenon, *i. e.*, a disaggregation of the colloidal micelles or a kind of peptization. To still others, and they are the most numerous, the phenomenon is chemical depolymerization of the hydrocarbon molecules. All these hypotheses fail to explain the most important fact, the part played by atmospheric oxygen.

Doubtless some investigators have suspected that oxidation takes place, but they have not realized its importance, nor have they been in a position to establish it as a fact.<sup>5, 46, 120</sup>

The idea that the plasticization of rubber by mastication is a result of oxidation began to be generally appreciated when in 1927 Fry and Porritt<sup>90</sup> showed that the

characteristic changes obtained by mastication can also be obtained by hot oxidation without mechanical treatment.

Park, Carson, and Sebrell<sup>103</sup> in 1928 made similar observations, but were less successful than Grenquist<sup>130</sup> in 1930 in that they overlooked the fact that oxygen plays a part in the phenomenon. On the other hand, Fisher and Gray<sup>181</sup> in 1926 showed that mastication in air saturates an appreciable part of the double bonds. This they attributed to oxidation.

It remained for Cotton<sup>142</sup> in 1931 and for Busse<sup>146</sup> in 1932 to prove independently and conclusively that oxidation is involved, and to demonstrate that, without it, mastication is incapable of plasticizing rubber. The conclusive experiment consisted in operating in a closed mixer filled with an inert gas (nitrogen, hydrogen, or carbon dioxide), under which conditions the rubber, even after prolonged mastication, *e. g.*, four hours, changed very little in consistency. When the inert gas was replaced by oxygen, Cotton found that the rubber softened more quickly than in air.

The oxidation which takes place under such conditions has an unsuspected activity, which Cotton and Busse have shown in different but equally ingenious ways. Cotton proved that, in spite of losses such as moisture and odoriferous volatile substances, the weight of the mass increased progressively with the time of milling except for the first few minutes. After two hours the gain in weight, which could be due only to oxygen, had reached 0.32 per cent, a value less than the true gain in weight, taking into account the losses mentioned. However, as has already been seen, such an addition of oxygen is fully sufficient to explain the softening.

Busse on his part proved the existence of autooxidation by detecting the presence of peroxides by the photographic process already described. Masticated rubber made a strong impression on a sensitive film. In this way the true agents of the softening, the peroxides, were detected directly, and the oxidizing emanations detected by Cotton close to the sheet of rubber as it leaves the rolls (emanations which he considered as coming from ozone) are also explained in this way. Finally the cause of the peculiar acidulous odor familiar to all who have carried on milling operations is now explained.

The two series of experiments supplement one another perfectly, and leave no further doubt about the nature of the phenomenon.

It is no less strange and unexpected to find such an intense form of oxidation, which is ten times as rapid as that of limonene, which oxidizes rapidly itself. In the case of rubber we are concerned with a substance which remains unchanged for years, and which after vulcanization requires months or even years to oxidize to any great extent. When masticated on a mill, this same substance absorbs in a few minutes as much oxygen as it does only after years in quiet contact with air. It is no exaggeration to say, as was done at the beginning of this paper, that the tendency of rubber to oxidize, ordinarily dormant, awakens at times in a disquieting way.

It is also none the less curious that a phenomenon of such magnitude should have remained unrecognized for so long a time, particularly in the face of the very significant fact that several investigators had previously gone to the effort of studying whether air has any action during milling. They too had tried to mill rubber in the absence of air but in an inert gas, but they were unsuccessful for the reasons already mentioned, *viz.*, the practical difficulty of excluding atmospheric oxygen. Furthermore, Cotton and Busse independently made it clear, either directly or by inference, that in spite of all care, the gas which they used was not strictly speaking free of oxygen, which will explain the slight softening found in the inert gases. In reality it is difficult to operate in the absence of air, and especially to assert rightfully that one has succeeded in doing this.

### Interpretation of the Phenomena

How is the extraordinary rate of oxidation during milling to be explained? First of all it cannot depend upon the heat developed mechanically, for there is no considerable heating except at the beginning, and the oxidation is nowhere nearly proportionate to the temperature thus attained. Finally technologists are well acquainted with the fact that the "breakdown" of rubber is more severe at low temperatures when the rolls are cooled artificially (cf. Griffiths<sup>237</sup>). It is not the breaking-down which facilitates the penetration of oxygen, in fact judged by the experiments of Venable and Fuwa,<sup>238</sup> Morris and Street,<sup>239</sup> and finally Williams and Neal<sup>132</sup> on the solubility of oxygen, this gas diffuses relatively quickly through the mass. Rubber stored in air is normally saturated with oxygen under the standard pressure of this gas in the atmosphere. Simple milling does not then add any more oxygen.

Cotton and Busse have each offered two explanations, one from the mechanical point of view, the other electrical. On the one hand, milling favors the attack of the molecules by oxygen, either by distorting them or by orienting them through slippage. On the other hand oxygen would be activated by the electrical charges at high potential which develop through friction. These charges are manifest as a glittering or as sparks, the crackling of which is at times confused with the bursting of air bubbles trapped in the mass. These electric charges are indispensable to mastication, for as noted by Shacklock<sup>131</sup> the suppression of this sparking, *e. g.*, by a jet of air, prevents plasticization.

Oxygen does not react in its ordinary molecular form, for as observed by Busse (*loc. cit.*), the reaction is no slower in the presence of antioxidants. The nature of the activation has not been identified. Perhaps the molecule must be first of all dissociated in order to react as individual atoms. Perhaps it must also be ionized in some still uncertain way. In any case, judged by the experiments of Cotton, which were confirmed later by Shacklock,<sup>148</sup> the intermediate active compound does not seem to be ozone.

One thing which seems probable is that the abnormal increase in the rate of oxidation is the resultant of several favorable factors. In addition to those which have been discussed, should not pressure be taken into consideration? The air bubbles, at the moment when they are squeezed between the mill rolls, cannot escape or elongate at will through a mass as tough and nery as rubber. They are therefore subjected to an enormous pressure, which certainly amounts to a great number of atmospheres, particularly in the case of small bubbles. Atmospheric oxygen is then dissolved forcibly and with an exceptional energy which is not attained in any other treatment to which rubber is subjected, not even in the Bierer-Davis bomb, because during milling there is agitation of the mass at the same time that the oxygen acts under pressure. This hypothesis finds support in the opalescence which appears after a certain time of milling, and which Cotton<sup>142</sup> (see Auer<sup>246</sup> as well) has attributed to tiny bubbles of gas, these bubbles being doubtless formed by excess gas which the mass, supersaturated at the time of milling, releases during rest.

### Conclusions

Returning now to an earlier subject, let us ask in what way the conversion of rubber to fatty substances differs from plasticization by milling. Both originate in the same way, *i. e.*, by the action of oxygen, and both are similar in appearance and in effects.<sup>90</sup> To distinguish the two phenomena, one must resort to an arbitrary point of view, *viz.*, that one phenomenon is spontaneous, whereas the other is induced. One is harmful, the other is advantageous, but fundamen-

tally, whether advantageous or disadvantageous, they are nothing more than one and the same change in the rubber. Whether the change is an advantage or a disadvantage depends upon when it happens and upon its extent. This will explain why milling is such a critical operation and is so difficult to control. Because plasticization is a conversion to fatty substances, which is stopped at the right time, the operations involved in practical milling are a delicate and dangerous process, a process the effects of which are attained not in years or even in months but in minutes. The least miscalculation, and disastrous results may be obtained.

Without entering into detail, it may be asked how many irregularities hitherto unexplained are from this time on readily explainable. The success of mastication depends upon peroxides, neither the quantity nor the behavior of which have so far been controlled, and even the existence of which has not until recently been suspected. It is a surprising fact that everything has always taken place in the desired way, particularly since to add to the complexity of things, the formation of peroxides itself depends upon electricity, and worse still upon the most changeable or capricious form, static electricity. Without suspecting it, one requires of a mixing mill that it perform the function of a generator of static electricity. Mixing is then at the mercy of influences which hinder the output of static machines, and it depends to some extent upon all kinds of indefinite factors, such as the state of the atmosphere, the temperature, the humidity and surface effects, not to mention the mixing mill itself, where nothing has been planned in advance to promote the unforeseen action.

Henceforth, with a knowledge of the mechanism of mastication, it is going to be possible to improve the various factors playing a part, and it does not require a great prophet to foresee within a short time a profound change in this century-old technique.

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# Fundamentals in the Problem of Resistance to Deterioration\*

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The problem of control in processes of deterioration is the problem of control of the speed of chemical reactions. The fundamental reactions in deterioration are oxidation processes involving oxygen, steam or other less universal oxidizing agents as well as reactions of polymerization, decomposition, and depolymerization. Heat and light, ionization, pressure, and the presence of accelerating agents are the important factors which influence the speed of such processes and are thus of major importance in a discussion of the fundamentals of the problem. Control of deterioration is the inverse of the historical occupation of the chemist. Since alchemical times his prime concern has been the promotion of chemical reactions. A belated attention to the problem of preserving his synthetic achievements is not, however, without its own peculiar scientific interest and practical significance.

## The Concept of Speed

Every chemist is familiar with the difference in reaction speeds of even essentially similar chemical processes. Thus, in the combination of hydrogen and oxygen to form water,  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ , high temperature, ultra-violet light, reaction surfaces or the electric discharge are necessary if reaction is to be achieved. And yet, in an entirely analogous molecular process,  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ , the reaction proceeds so rapidly at ordinary temperatures that the brown fumes of the product are visible immediately after mixing. Such comparisons indicate that the velocity with which a chemical process occurs is dependent on some factor additional to that of concentration. The concentration determines the frequency of collisions between the reactants. But chemical reaction does not normally occur at every collision. Reactions which behave thus are liable to be explosive in nature. In all ordinary chemical reactions there is a collision efficiency factor which is of controlling importance in most cases since, in the majority of actual chemical operations, the variations in the concentration factor are not large. An example may serve to illustrate these points. The combination of two hydrogen iodide molecules to form hydrogen and iodine  $2\text{HI} = \text{H}_2 + \text{I}_2$  occurs measurably fast at temperatures in the neighborhood of  $300^\circ \text{C}$ . From kinetic theory it is possible to calculate the number of collisions that occur between two molecules under any given conditions of concentration and temperature by means of the equation:

$$z = 2 \sqrt{2} \pi \frac{n_1 n_2}{v^2} \left( \frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2} \cdot kT} \quad (1)$$

where  $n_1$  and  $n_2$  are the numbers of any two types of colliding molecules in volume  $v$ , with collision diameters  $d_1$  and  $d_2$ , and molecular masses,  $m_1$  and  $m_2$ ,  $k$  being the Boltzman constant. For like molecules colliding<sup>1</sup> this reduces to:

$$z = \frac{n^2 d^2}{v^2} \sqrt{\frac{4 \pi kT}{m}} \quad (2)$$

\* Edgar Marburg Lecture before the Annual Meeting of the American Society for Testing Materials, Atlantic City, N. J., June 22, 1932.

A comparison of the collision numbers so calculated and the actual number of reacting molecules indicates that at a temperature of  $600^\circ$  Abs. ( $327^\circ$  C.) the collision efficiency factor is only  $10^{-16}$ , a very small number. This efficiency factor changes rapidly with temperature but at a temperature of  $781^\circ$  Abs., where the velocity of reaction is almost too rapid to measure conveniently, the ratio of effective to total collisions is still only  $10^{-12}$ . Indeed we may state as a general rule that in a temperature and pressure range where molecular reactions are easily measurable the order of magnitude of effective collisions is one in a million million total collisions. The rate of a reaction,  $k$ , is the product of the total number of collisions and the efficiency factor. Since this latter varies with temperature it has been found possible to express it as a function of the absolute temperature of the form  $e^{\frac{-E}{RT}}$  so that the velocity equation is:

$$k = z \cdot e^{\frac{-E}{RT}} \quad (3)$$

where  $z$  is the total number of collisions given by Eq. 1 or 2, and the efficiency factor is an exponential in terms of the absolute temperature,  $T$ , the gas constant,  $R$ , and

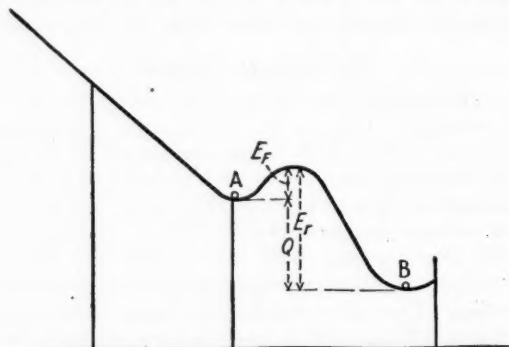


Figure 1—Roller Coaster Model to Illustrate Activation Energy

an energy quantity,  $E$ , which we may term the activation energy, a characteristic quantity for each reaction. The smaller the value of  $E$ , obviously, the faster will a reaction occur at a given temperature. Or, returning to our two reactions,  $2H_2 + O_2 = 2H_2O$  and  $2NO + O_2 = 2NO_2$ , we can say that the activation energy of the former is very much larger than that of the latter.

**Activation Energy.**—Some twenty years ago an explanation of this inefficiency of collisions and of the accelerating effect of temperature was formulated. The conclusion was reached that only those collisions whose joint energy exceeded a certain definite minimum of energy would result in chemical change. This energy, which we have called the activation energy, is attained the more frequently the higher the temperature, and, according to kinetic theory calculations, in just the relationship given above and required by the experimental observations on the effect of heat on speed of reaction. The activation energy, then, is the minimum energy which an atomic or molecular system in its initial state must achieve over and above the average energy of that state in order to pass to the final state of reaction product.

The process may readily be illustrated with the aid of a miniature roller coaster

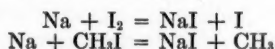


and a pair of marbles (Fig. 1). With small energy increments due to collisions the system will remain in the energy valley, *A*, of the reactant molecules. The greater the violence of the collisions the more probable the attainment of energy sufficient for one to pass over into the energy valley, *B*, which represents the reaction products. The model also shows that the minimum energy necessary is less for those reactions which occur with evolution of energy. (Transitions on the roller coaster from higher level, *A*, to lower level, *B*.) It is greater for the reverse process which occurs with an absorption of heat by an amount equal to this energy difference, *Q*, between the initial and final states:

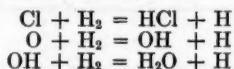
$$E_r - E_f = Q$$

where *r* represents reverse and *f* forward. The higher the activation energy required the more violent the collisions required, or what is the same thing, the higher the temperature necessary for a given speed of reaction.

**Reactions Involving Atoms and Radicals.**—Reactions between molecular species require in general marked activation energies; their collision efficiencies for reaction are, as already stated, low. During the past decade, experimental and theoretical research has shown that interactions between atoms or radicals and molecules possess a very much higher order of collision efficiencies. Many reactions between atomic species and molecules occur practically at every collision. Thus, Polanyi and his coworkers<sup>2</sup> studied a series of reactions between alkali vapors and the halogens and alkyl halides as, for example:



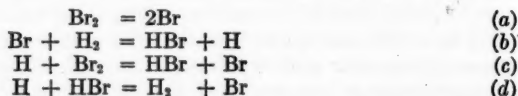
Since these "elementary reactions" occurred at every collision a special technique involving studies at micropressures was necessary. The reactions were slowed down in tempo by reducing the concentration term in Eq. 3. Polanyi's first results indicated that, whenever the "elementary reaction" was exothermic, such reactions in general occurred on every collision. More recently it has been shown that this rule is not completely general. Thus, the interaction of sodium vapor and methyl fluoride,  $\text{CH}_3\text{F} + \text{Na} = \text{NaF} + \text{CH}_3$ , although markedly exothermic, is, nevertheless, slow and requires a marked activation energy ( $> 20,000$  cal.). Atomic reactions involving hydrogen molecules as, for example:



while exothermic in character do not occur at every collision the three examples cited requiring activation energies of the order of 5 to 10 kg.-cal. When such reactions are endothermic in nature as, for example, the interaction of bromine atoms and hydrogen molecules,  $\text{Br} + \text{H}_2 = \text{HBr} + \text{H} - 17$  kg.-cal., the activation energy of the reaction cannot be less than 17 kg.-cal. and may be a few kilogram calories greater than this value.

The importance of such atom or radical reactions lies in the possibility of their being intermediate stages in the process of reactions between molecules. This was suggested by Nernst in his discussion of the hydrogen-chlorine photochemical reaction, according to which, with the light absorption producing two Cl atoms from an absorbing  $\text{Cl}_2$  molecule, a sequence of rapid reactions,  $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$  and  $\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl}$ , was possible. This suggestion of an atomic chain became, as we shall see, fundamental in the discussion of reactions, many of which are of importance in problems of deterioration. The practically simultaneous

suggestion by Christiansen, Herzfeld, and Polanyi of a similar atom chain mechanism for the thermal combination of hydrogen and bromine in which the sequence of reactions is:



extended the idea of such rapid intermediate atomic reactions to thermal processes. Reaction (b) of this sequence is the endothermic reaction already discussed which, with bromine atoms produced by light absorption, determines the effect of temperature on the whole reaction. Reaction (d) accounts for the inhibitory action of hydrogen bromide on the reaction, a factor discovered by Bodenstein and

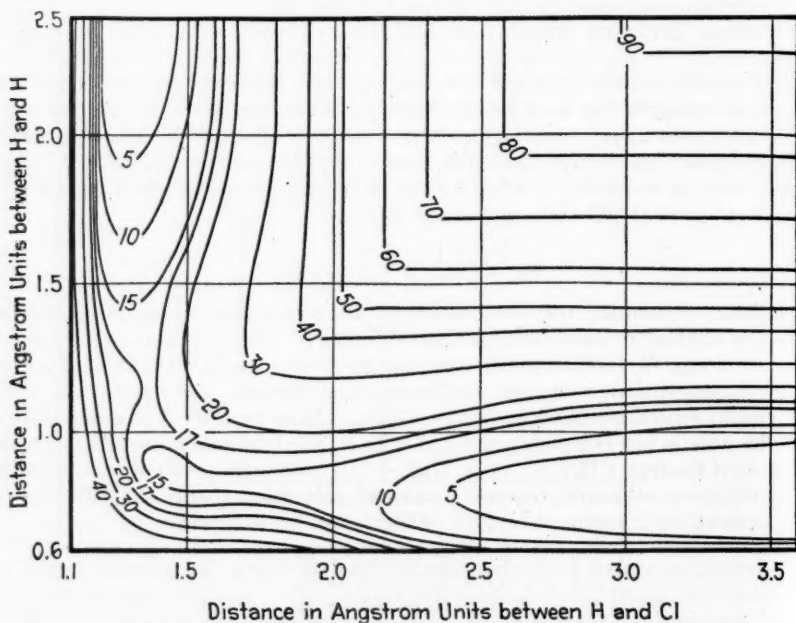
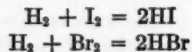


Figure 2—Potential Energy in Kg.-Cal. of the System H-H-Cl

Lind<sup>2</sup> in their much earlier experimental studies but unexplained by them and not understood prior to the formulation of the atomic chain mechanism. This mechanism provided the explanation for the differences between the kinetics of the two reactions:



Whereas the former is a simple bimolecular collision reaction, the latter does not so occur because the activation energy of the bimolecular collision reaction is much higher than that of the alternative atomic chain mechanism cited above. The path from the initial to the final state, which involves the lower activation energy, is the preferred path and will occur more frequently.

It is pertinent here to call attention to newer methods of approach to this prob-

lem of velocity of chemical processes because they are beginning to yield methods for the *calculation* of velocities of reaction, at any rate in the simpler atomic and molecular processes.

The accepted concepts of atomic structure now make possible a determination of the mutual potential energies of atomic systems. For two atoms, we can, with Franck and Condon, set up from spectroscopic data a potential energy curve representing the mutual attraction and repulsion of two atoms,  $A$  and  $B$ , at varying distances apart. These attractions and repulsions will be modified by the proximity of a third atom,  $C$ , to an extent now calculable from quantum mechanical bases. By making such computations and the similar calculations for a molecule,  $AC$ , with approaching atom,  $B$ , it is possible to compute the potential energy of the system of atoms,  $A$ ,  $B$ , and  $C$ , at any distances of the three from each other. We can embody the results of such a study in a potential energy surface, the form of which can readily be seen from the accompanying contour map (Fig. 2). A glance will show what is the easiest pathway which the system  $AB + C$  can take in order to reach the end system  $AC + B$ . The easiest path so far as energy content is concerned is along the valley route between the precipitous hill slopes on each side. An examination of the contour of this valley floor indicates, first, a gentle rise, the activation energy of the reaction  $AB + C$ , secondly, a shallow trough corresponding to a possible compound  $ABC$  but so shallow that the energy of the system in motion is more than adequate to carry it through the trough over a tiny saddle once more to the final end state  $AC + B$ . The progress of a marble along this valley floor faithfully imitates the behavior of such an atomic system. More recently Eyring and his associates<sup>4</sup> have extended this method to more complex reactions between molecules.

Such calculations abundantly verify the conclusions which we have just reached. Thus, in the hydrogen-bromine combination, the bimolecular collision process is found to have an activation energy greater than 43,000 cal. The atomic chain mechanism is known to be less than 30,000 cal. With iodine and hydrogen the reverse is true, calculations indicating that the atomic chain mechanism requires 18,000 cal. larger activation energy. Perhaps, however, the most striking result from the calculations is the very definite conclusion that hydrogen and fluorine molecules do not react at room temperatures and that even fluorine atoms would show little reactivity with hydrogen molecules at room temperatures. This conclusion is very emphatically contradicted by all the textbooks of inorganic chemistry, but the textbooks are wrong and have been so for the generations that have elapsed since the original Moissan-Dewar experiments. For, as has recently been shown by von Wartenburg and his associates,<sup>5</sup> neither atomic nor molecular fluorine, *when pure*, show any reactivity toward hydrogen at ordinary temperatures. The slowness of reaction between sodium vapor and methyl fluoride, which we have already discussed, is a parallel case of slow reaction velocity in fluorine compounds.

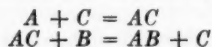
These general remarks on the incidence of atomic reactions in processes which, in their summation, involve reactions between molecules and may, by their occurrence, increase the speed of such processes, have been introduced into the present discussion because it will emerge that many of the reactions involved in processes of deterioration are such that chains of rapid reactions involving atoms or radicals may play an important role. Procedures designed to minimize the occurrence of such reactions, or their suppression if inevitable, are an essential part of the technique involved in the control of deterioration.

**Relative Effects of Collision and Efficiency Factors.**—A change in the velocity of chemical reaction at a given temperature can be secured, as Eq. 3 shows, either by a modification of the collision factor,  $z$ , or the activation energy,  $E$ .

Of these two factors the latter is by far the more important in its influence on velocity. Examination of Eqs. 1 and 2 will reveal that the only possible variable in  $z$  at constant temperature is the concentration term,  $\frac{n_1 n_2}{v^2}$ . Since the concentration appears (for a bimolecular reaction) as the square, it follows that changing the pressure in a gas reaction (the worst case) to 0.001 or to 1000 atmospheres, only influences the velocity by a factor  $10^{-6}$ . With liquid or solid systems the variation in  $\frac{n_1 n_2}{v^2}$  would be considerably less. On the other hand, by reducing the activation energy,  $E$ , or by raising the temperature,  $T$ , Eq. 3 shows that an exponential change may be secured in the value of  $k$ , the velocity of reaction. Thus, for example, if a bimolecular reaction with an activation energy  $E$  of 40,000 cal. and occurring negligibly at room temperatures ( $T = 300^\circ \text{ Abs.}$ ) be converted into a sequence of reactions of which the maximum activation energy of the constituent steps was only 10,000 cal., a change in velocity equal to  $e^{\frac{-(40,000 - 10,000)}{RT}}$

$$= e^{\frac{-30,000}{600}} = e^{-50} = 10^{22} \text{ fold would result.}$$

**Activation Energy Lowered by Catalysts.**—The resolution of a reaction into a series of steps, each with an activation energy markedly inferior to that of the single stage process is, in reality, the objective pursued in a search for a catalyst for a reaction. Thus, if a reaction,  $A + B = AB$  with an activation energy  $E_1$  at a temperature  $T$  can be resolved with the aid of a catalyst  $C$  into two steps,



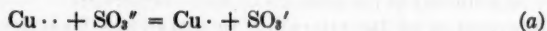
with activation energies  $E_2$  and  $E_3$  markedly less than  $E_1$ , then, as the numerical example just cited shows, enormous changes in the rate of reaction can be secured.

**Surfaces.**—As is well known, surfaces are excellent agencies for securing such stepwise attainment of slow reactions. An index of the efficiency factor of a surface in the promotion of chemical reactions may be obtained by a consideration of a reaction recently studied by Pease at Princeton both as a homogeneous collision gas reaction (activation energy,  $E$  homogeneous = 43,000 cal.) and also as a surface reaction in contact with copper. The reaction is the simple one just discussed,  $A + B = AB$ , hydrogen and ethylene forming ethane. The collision reaction proceeds at  $500^\circ \text{ C.}$  at about the same speed as the surface reaction at  $0^\circ \text{ C.}$  From the activation energy of the high temperature process we are able to calculate from the data of Pease how fast the reaction would proceed by collision at the temperature of  $0^\circ \text{ C.}$  at which it proceeds measurably rapidly on the copper surface. The result is illuminating. The presence of the copper produces an acceleration of the simple collision process of the order of 10 million, million, millionfold. This example represents a small, rather than a high, surface efficiency. The azo-bacter, a bacterium which fixes the nitrogen of the air at room temperatures possibly operates by a surface process analogous to ammonia synthesis. If this be true one can compute that the acceleration produced by such bacteria over the normal rate of gaseous collision reaction must be of the order of  $10^{72}$  or one million raised to the twelfth power.

These surfaces operate by splitting a reaction with high activation energy into a number of successive steps each of which has a characteristic activation energy markedly smaller than that of the simple process. The longer path is the more speedy because the increments of energy at each step are less. The analogy of the zigzag path up the mountain face instead of the direct assault conveys something of the idea involved.

Recently, Sherman and Eyring<sup>6</sup> have made a theoretical calculation, which accords with practical experience, that the tearing apart of the two atoms in a molecule of hydrogen, a process which ordinarily would require 100,000 cal. of energy per mole, and is normally achieved only on high-temperature tungsten filaments or in the atomic hydrogen torch or by means of a high-tension discharge, is achieved at room temperatures and even at lower temperatures on suitably spaced carbon atom surfaces with less than one-tenth of the activation energy required for the homogeneous gaseous process. Thus achieved, the hydrogen atoms obtained are not free, but are attached to the carbon surface, with only, however, approximately one-half the energy with which they were bound to one another in the molecule. This follows from the observation that the heat of adsorption on the surface is very small. By reason of their weaker binding to the carbon atoms than to one another in the molecule, the greater potential reactivity of hydrogen atoms at such a surface arises.

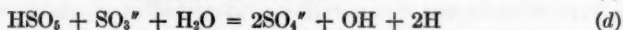
*Homogeneous Catalysts.*—The ideas outlined already with respect to the influence of surfaces on the activation energy of chemical reactions are equally applicable to reactions in homogeneous media. The substitution, for a reaction with high activation energy, of a stepwise series of reactions leading to the same end point, the steps each having markedly lower activation energies, will produce a marked increase in reaction velocity. As an example of this kind we shall choose a reaction which for other reasons also is fundamental in the problem of deterioration; we refer to the oxidation of sodium sulfite. It has been definitely established by the work of Titoff<sup>7</sup> that in solutions of the highest purity, the oxidation of sodium sulfite by dissolved oxygen is negligibly small. In the present terminology the reaction possesses a relatively high activation energy. Titoff, however, was able to show that the oxidation process was enormously accelerated by extremely minute amounts of various ions, the most notable example being the copper ion, which, even in a concentration as low as  $10^{-13}$  molar, produced a perceptible acceleration of the oxidation of such solutions. The mechanism of the action of the copper ion has recently been set forth by Haber and his associates in a comprehensive series of investigations,<sup>8</sup> dealing with various aspects of the autooxidation problem. The action of the cupric ion is to interact with the sulfite ion to form the ion  $\text{SO}_3'$  of a weak acid,  $\text{HSO}_3'$ , which, as it represents one-half of the acid dithionous acid, may be termed monothionous acid. The equation for its production would read:



The stable form of this univalent ion is its dimer the dithionate ion:



and dithionate is the major product of the interaction of cupric ions and sulfite ions in the absence of oxygen, as was early shown by Baubigny.<sup>9</sup> With dissolved oxygen present in the system, the formation of dithionate ion by dimerization, owing to the low concentration of  $\text{SO}_3'$  and the consequent low probability of encounter between two such ions, is subordinate to the interaction of the monothionous acid with oxygen to form  $\text{HSO}_3$  and the reaction of the latter with  $\text{SO}_3''$  to form  $2\text{SO}_4''$ , thus;

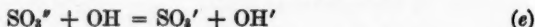


Reaction (c) will have a low activation energy because of the radical-like character of the  $\text{HSO}_3$ . The moloxide formed,  $\text{HSO}_3$ , is assumed to possess in common with other moloxides a tendency to rapid reaction.



Haber supports the mechanism proposed by demonstrating that all reaction conditions which in presence of dissolved oxygen favor sulfate formation yield, in the absence of oxygen, dithionate. Oxidation agents such as hydrogen peroxide, potassium persulfate, and potassium permanganate accelerate autooxidation and also yield dithionate in absence of oxygen. Dithionate is also formed at unattacked anodes on electrolysis of sulfite solutions and, similarly, oxygen consumption by sulfite solutions in the anode compartment during electrolysis is markedly greater than in the absence of electrolysis. Similarly, ultra-violet light absorbed by sulfite solutions increases enormously the oxygen absorption and also produces dithionate in absence of oxygen.

One feature of fundamental significance in the problem of sulfite oxidation, to be dealt with more in detail in subsequent sections, may be exhibited before the discussion of this reaction is closed. An examination of reaction (d) above indicates that the sulfate ion formation is accompanied by the simultaneous formation of the hydroxyl radical. It must be pointed out that the rapid interaction of this highly reactive radical with a sulfite ion according to the equation



regenerates an ion of monothionic acid such as was produced with the aid of the cupric ion in reaction (a). Such an ion may obviously repeat the cycle (c), (d), and (e) either indefinitely or until one of the stages in the cycle is rendered impossible by alternative reactions. Reaction (b) of our scheme is one such alternative which would break the sequence. It is, however, evident that, by a sequence of reactions which are self-perpetuating, a whole cycle of processes may succeed an initial impulse provided by the cupric ion. We shall see, in the sequel, that such reactions, the so-called "chain reactions," are by no means infrequent in the problems of deterioration. Their existence multiplies the accelerating effect due to the presence of the reaction initiator—in this case the cupric ion. It should be emphasized, however, that the existence of a chain mechanism is not a necessary concomitant of a reaction sequence which occurs with lower activation energy and hence more rapidly than the uncatalyzed reaction. There are many reactions which do not involve chains, in which the presence of an active agent, whether a surface or homogeneously distributed throughout the reaction medium, brings about a succession of reactions with a given end point more rapidly than the same process can be achieved in the absence of such accelerants.

**Prevention of Deterioration in Catalyzed Reactions.**—The problem of the prevention of deterioration in such systems is the problem of ensuring the effective absence of such surfaces or homogeneous catalysts as may initiate the faster reaction sequence. We may term this type the *inhibition of deterioration by reduction of the concentration of a positive catalyst*. At one time it was very generally believed that this constituted the sole method by which reduction in the speed of chemical change and, more specifically, the prevention of deterioration could be secured. The subsequent sections will indicate that this is far from correct. Nevertheless, this category of preservation is an important one, as the discussion of examples will subsequently show. Many materials may be successfully protected against deterioration by removal of all materials which permit a reaction path of lower activation energy than the deterioration reaction itself possesses. In general this type of catalyzed deterioration is identified in all those cases in which progressive purification of the desired material leads to a progressively increasing permanence.

**Inhibition of Reactions by Lowering the Concentration of a Reactant.**—We may now consider briefly the category of inhibition phenomena in which re-

action is suppressed by reduction in the concentration of a reacting species. As earlier noted, there are theoretical reasons why such methods involving as they do the  $z$  factor of Eq. 3 may not be so pronounced in their efficacy as methods just discussed involving the activation energy. It is obvious, however, that a process of deterioration involving oxidation by atmospheric oxygen may be diminished in its incidence by any arrangement which ensures that the concentration of atmospheric oxygen accessible to the material shall be reduced, if possible, to a minimum. The simple device of storing oxidizable analytical solutions in an atmosphere of an inert or reducing gas is one illustration of this procedure. The coating of an oxidizable film with a covering impervious to oxygen is another illustration.

An important group of reactions to which the method of reduction of concentration of a reacting species is applicable is that in which one of the reactants undergoing change is the ion or molecule of an electrolyte. If the ion be the more reactive, the undissociated electrolyte being either non-reactive or of a lower order of activity than the ion, inhibition will occur whenever any substance is added to the system which represses the dissociation of the electrolyte whose ion is reactive. Conversely, in any reaction in which the undissociated electrolyte is more reactive than its ions, inhibition will occur when, to the reaction system, substances are added which will increase the electrolytic dissociation. If, in a reaction of either type just mentioned, an inhibitor of this kind results from the reaction the system will show auto-inhibition or auto-retardation. But the converse is also true, and a product may result which accelerates the change, in which case addition of substances designed to suppress the concentration of a catalyst is necessary.

The hydrolyses of halogen substituted organic acids are examples to which the considerations just discussed apply. Hydrobromic acid inhibits the hydrolysis of bromosuccinic acid, evidently because the ion is more reactive than the undissociated molecule. The retardation is inversely proportional to the hydrobromic acid concentration.<sup>10</sup> The same action of hydrogen halides is observed in the hydrolysis of the several halogen acids of acetic, propionic, and butyric acids.<sup>11</sup>

**Light-Sensitive Processes.**—Many reaction systems relatively quite stable in the dark undergo chemical change when exposed to light. It is the absorbed light which is the source of the activation energy of the system. This does not mean that all light absorbed will produce chemical change. The stability of numerous colored materials is proof of this. Of the total light absorbed only certain regions of absorption may produce chemical change. The type of change may be dependent also on the nature of the light absorbed. Thus, one region may produce oxidation reactions, another decomposition or polymerization.

The simplest cases of photo-change are those in which there is a one-to-one relationship between the light energy absorbed and the chemical change produced. The light energy is measured in terms of quanta of monochromatic light, each equal to  $h\nu$ , where  $\nu$  is the frequency or reciprocal wave length of the light and  $h$  is the quantum constant =  $6.55 \times 10^{27}$  erg seconds; the chemical energy is expressed as the number of molecules reacting. Each molecule receiving a quantum of light energy becomes activated and enters upon its characteristic chemical change. In all such cases, the only method available to prevent the process occurring is the physical method of suppression of the light energy absorption. This may be accomplished by external light filters. Glass filters are useful when it is merely a question of preventing the access of visible light. The use of suitably colored glasses, for example brown or yellow glass, is resorted to in case the blue or violet region of the spectrum is active. It may be that a substance can be added to the reaction system which absorbs in that region of the spectrum to which the reactant is sensitive. The foreign substance may dissipate the light it absorbs without trans-

fering the energy to the reactant, thus acting as an "internal light filter." Examples of this type of screening effect were noted by Anderson and Taylor<sup>12</sup> in studies of the inhibition of hydrogen peroxide decomposition. It was shown, however, in many of the cases studied that the inhibitors acted more efficiently when in the peroxide solution than when in a screening solution of equivalent thickness and concentration. This is doubtless to be associated with the chain characteristics of peroxide decomposition subsequently to be discussed. Alyea and Jeu<sup>13</sup> have recently suggested that a screening effect may be found within the reacting molecule itself, as, for example, in the photochemical decomposition of acetaldehyde into carbon monoxide and methane. Two absorption bands are known: one, involving the  $\text{CH}_3$  group has its maximum well below 2000 A. U., the other has a maximum at 2800 A. U., the absorption falling to negligible amounts below 2200 A. U. In the region 2400 to 2200 A. U., both types of absorption occur but only the  $> \text{CO}$  absorption leads to decomposition. Since, at 2200 A. U., most of the absorption is by the  $\text{CH}_3$  groups, these radicals may be acting as internal light filters, robbing the  $> \text{CO}$  group of the light which it might use to decompose the molecule. Alyea and Jeu suggest that such an intramolecular screening may be operative in the photopolymerization of vinyl acetate studied by Taylor and Vernon<sup>14</sup> where low quantum yields were obtained at 2300 and 2536 A. U., whereas in the region 3000 to 4000 A. U. high quantum yields, averaging 1000 molecules polymerized per absorbed quantum, were obtained.

An important example of photo-deterioration, which belongs to the category under discussion, is the decomposition of nitrocellulose film by light. The best available evidence indicates that the quantum yield, the number of molecules decomposed per light quantum absorbed, is unity or less. Hence, screening or physical protection appears to be the only possible method at present for stabilizing such film against light action. Use has already been made of protective coatings of waxes containing light-absorbing materials. A variety of photo-reactions occur, in part dependent on the wave length, which profoundly modify the film characteristics.<sup>15</sup> The film becomes acid, its brittleness increases, its tensile strength decreases, a yellow color develops. The change in the colloid is profound since the viscosity of a solution of irradiated film is lower than that of the solution from which the film was cast. Extended irradiation may yield material without marked influence on the viscosity of the solvent medium.

In the extreme ultra-violet light from 1900 to 2600 A. U., the reactions occurring are decomposition reactions which materially reduce the film thickness. The absorption of such light by the film is very strong and hence the action of the light is confined to the surface of the film. Acidity develops in the film with light from 2300 to 6000 A. U. with a strong maximum around 3130 A. U. In this region the absorption is more moderate so that the acid-forming decomposition is distributed throughout the film. Brittleness is most markedly produced by light in the region around 2537 A. U., very much more rapidly than by the longer wave lengths. The long wave length region from 2300 A. U. upward produces an increased solubility of and imbibition by the film.

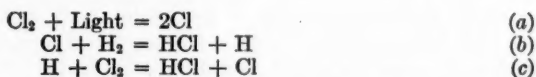
One aspect of the use of "internal light filters" by incorporation of the absorbing material within the body of the material to be protected must here be emphasized. Use of an internal light filter is effective only if the energy absorbed by the added agent can be dissipated without transfer to the reactant. The phenomenon of "photosensitization," familiar to the photographer in the production of panchromatic and orthochromatic film, indicates that a material may be sensitized to light otherwise ineffective by incorporation of light absorbing materials in the reaction system. The added agent absorbs and transfers the energy to the reactant. This

accounts for numerous observations; for example, in the case of nitrocellulose deterioration, where incorporation of suitable light absorbing materials not only does not slow down the process of deterioration but actually accelerates the decomposition.

The use of acetate film or cellulose ethers offers the possibility of diminishing the discoloration obtaining with exposure to light, since this is in major part associated with the nitro-content of nitrocellulose. The experiments just recorded suggest, however, that brittleness of such films will still occur on subjection to light action, any advantage which they might show being a function of their smaller light absorption. The observation by Doree and Dyer<sup>16</sup> that cellulose, under the influence of ultra-violet light, is converted to oxycellulose with great loss of tensile strength is also evidence in support of this point of view.

**Photochemical Chain Reactions.**—A fundamentally different set of conditions exists when the reaction initiated by light absorption is succeeded by a whole chain of thermal chemical reactions, a condition which is revealed by a considerable excess of molecules undergoing change per unit quantum of light energy absorbed, the quantum yield of the process. Under such conditions, the efficiency of any physical screening process is multiplied by a factor equal to the quantum yield of the light screened out. In addition, however, there exists a possibility of reducing the net change occurring, not by physical screening, but by suppression of the sequence of chemical processes succeeding the initial light absorption by incorporating an inhibitor in the material undergoing change. This development of the past twenty years involves so many reactions of both technical and scientific interest and has given so definite an orientation to the problem of prevention of deterioration that an extended treatment may be permitted.

Bodenstein<sup>17</sup> in 1913 pointed out that as many as  $10^6$  molecules of hydrogen chloride might be produced for every quantum of light energy absorbed by chlorine in admixture with hydrogen. He also emphasized that the yield was dependent on the purity of the gas mixture and could be markedly diminished by the presence of impurities such as oxygen, nitrogen-containing compounds such as ammonia, proteins, and the like. His early efforts to formulate a chain or succession of reactions to account for the high yield from an initial light impulse were superseded by a mechanism postulated by Nernst in 1916:



and so on by repetition of reactions (b) and (c). On such a basis inhibitors must act by destroying the H or Cl atoms which are the essential links in the chain. The Nernst mechanism still survives, at the present time, in spite of numerous doubts raised at intervals, as the best formulation of the hydrogen chloride chain.

The possible effectiveness of an inhibitor in such a reaction can easily be indicated. If, in a pure gas mixture, the chain reactions succeeding an initial light impulse were  $10^6$  in number, it is evident that the added agent which would interact with and remove from the system the first hydrogen atom formed in reaction (b) would reduce the hydrogen chloride yield 1,000,000 fold. A 100 per cent efficient trap for chlorine atoms in reaction (a) would suppress hydrogen chloride formation entirely. If it acted only on the chlorine atom produced in reaction (c) the yield would be reduced 500,000 fold. The earlier the inhibitor intervened in the reaction chain sequence the greater the proportionate reduction in reaction velocity and the greater its efficiency as an inhibitor. The longer the reaction chain, the greater



the possible influence of an inhibitor in diminishing the reaction rate. The maximum reduction possible is to a rate equal to the reciprocal of the chain length.

**Chain Reactions and Retardation.**—It was pointed out by Christiansen<sup>18</sup> that the existence of chain reactions, whether initiated thermally or photochemically, was indicated in all cases in which a minute amount of added material produces a marked diminution in reaction velocity. He pointed out that an inhibitor in small concentration could not affect either the collision factor,  $z$ , nor the activation

energy or efficiency factor,  $e^{\frac{-E}{RT}}$ , of Eq. 3. A chain mechanism of the type just discussed would, however, offer the possibility of such inhibitory power of a minute quantity of material, the inhibition being the more marked the longer the reaction chain, the efficiency of the inhibitor being determined by the stage in the chain at which it intervened, the earlier the more efficient. As we have already pointed out, a retardation might also be achieved by an inhibitor reducing the concentration of a powerful accelerator of reaction, which, in the case of reactions involving chains, might be spoken of as chain initiators. It will emerge that a distinction between these two possible modes of retardation can be achieved.

An ordered file of dominoes, arranged one behind the other at suitable intervals, provides a means of illustrating the concept of chain reactions. With the dominoes properly spaced an impulse communicated to the first will suffice to convert the whole row from the upright to the oblique position. It is the energy of the change which is the source of the activation energy of the succeeding change. Such initial impulses can be supplied by light energy, by ionization (alpha particles, electric discharges), by accelerators or catalysts or by an energetic collision between two energy-rich molecules. It is evident that in these last, the purely thermal processes, the velocity of reaction will be as many-fold, calculated on the basis of collisions with a given energy of activation, as there are chain members succeeding the initial activation process. Some thermal explosions are of this type. The intervention of an inhibitor in a reaction chain can be illustrated by the insertion of a rigid peg somewhere between the dominoes in a given row. If it intervenes early in the chain it represents a good inhibitor; if late, a poor one.

**Chain Processes in Autoxidation Chain Reactions.**—That very many secondary chemical processes may succeed an initial activation, either by light or heat, even in liquid systems has been convincingly demonstrated by Bäckström<sup>19</sup> in cases of autoxidation such as the oxidation of sodium sulfite solutions and of aldehydes such as benzaldehyde. Bigelow<sup>20</sup> had long ago shown that the thermal oxidation of sulfite solutions was susceptible to inhibition and, as already stated, this was coupled by Titoff with the extraordinary sensitivity to acceleration by minute amounts of accelerating agents such as copper ions. The photochemical oxidation was found by Matthews and Dewey<sup>21</sup> and Matthews and Weeks<sup>22</sup> to be faster than the thermal reaction, and also inhibited by a variety of added agents. The chain character of the reaction followed from Bäckström's photochemical yield measurements, as many as 50,000 molecules of sodium sulfite reacting per absorbed quantum of light of wave length 2536.7 Å. U. even in 1-molar solutions. Bäckström established a link between the thermal and photochemical reactions by his observation that alcohols affect both rates of reaction alike, the relative rates in presence of such inhibitors being satisfactorily represented in both cases by the equation:

$$V = \frac{k_1}{k_2c + k_3}$$

where  $c$  is the concentration of inhibitor, the constants  $k_2$  and  $k_3$  being common to



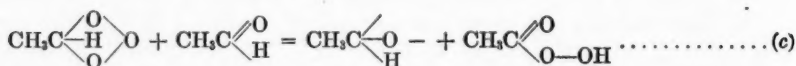
both thermal and photochemical reactions,  $k_1$  varying according as the reaction was thermal or photochemical, being dependent on the rate of activation or formation of the initial stage in the chain process. The inhibitor constant,  $k_2$ , is specific for a given inhibitor. The presence of  $k_2$  indicates the possibility of ending chains other than by an added inhibitor. Its importance diminishes the more important inhibition by the added inhibitor,  $k_{2c}$ , becomes.

**Mechanism of Inhibitor Action.**—The correctness of these general conclusions and the mechanism of inhibitor action in this particular case were established later by Alyea and Bäckström.<sup>23</sup> The inhibition involves an induced oxidation of the inhibiting alcohol, a molecule of the oxidation product (aldehyde or ketone) being formed whenever a chain is broken. The experimental results which support this conclusion may be summarized. At low alcohol inhibitor concentrations, the amount of alcohol oxidized increases with increasing alcohol concentration. At high inhibitor concentrations the amount of alcohol oxidized per unit time is constant, independent of its concentration, in both the thermal and photochemical reactions. In this latter concentration region, the number of inhibitor molecules oxidized per unit time is quantitatively the same for different alcohols of widely different inhibitory powers. Two alcohols present in a solution have an additive inhibitory effect and are oxidized in the ratio of their inhibitory powers; the total number of alcohol molecules oxidized is, however, the same as when only one alcohol is present. All these facts are explainable on the assumption that with sufficient alcohol present as inhibitor each chain process started is stopped by an alcohol molecule, the number of which molecules oxidized is a quantitative measure of the number of reaction chains initiated. Alyea and Bäckström showed that the number of secondary processes, the links in the chain, was the same in both thermal and photochemical reactions and is equal to the efficiency (molecules per quantum) as determined photochemically. They also found that copper sulfate accelerated the thermal reaction without altering the ratio of sulfite oxidized to alcohol oxidized. This means that the catalyst and inhibitor act independently. The catalyst initiates the chain process, the inhibitor quite independently breaks the chain of secondary reactions. The mechanism in this case was definitely not a case of inhibition by suppression of the concentration of a catalyst.

The autooxidations of many organic compounds show similar chain mechanisms. The oxidation of benzaldehyde and cinnamaldehyde were shown by Bäckström to be of this type. As many as 10,000 molecules of benzaldehyde were oxidized per quantum of light energy absorbed. As with sulfite solutions, these oxidations may also be accelerated by catalysts, as, for example, manganese salts, though even benzaldehyde purified by many distillations in an atmosphere of carbon dioxide shows autooxidation.<sup>24</sup> Bäckström and Beatty<sup>25</sup> showed that, as in the case of sulfite, the inhibitory action was associated with an induced oxidation of the inhibitor, anthracene in the case studied. The primary oxidation product was anthranol which was autooxidizable, reacting with oxygen to give a peroxide which later slowly decomposed with the formation of the final reaction product anthraquinone. With increasing anthracene concentration the relative amounts of oxidation products formed approaches one mole of benzoic acid per mole of anthraquinone. The course of the reaction shows that the induced oxidation of the anthracene is the result of a reaction with a peroxide of benzaldehyde, but it may be shown that this reaction cannot be attributed to the stable form of this peroxide, benzoperacid. Side reactions occur also to minor degrees producing both anthrahydroquinone and also unidentified and complex colored products. The anthracene also plays the part of a screening material in the light reaction. These functions of anthracene are illuminating in view of the use of this reagent in the suppression of gum

formation in cracked gasolines especially where these latter are exposed to light action in the visible-type gasoline stations.

The unstable intermediate peroxide is also assumed by Bodenstein<sup>26</sup> to account for the kinetics of the oxidation of gaseous acetaldehyde, the kinetic treatment developed being also applicable to the oxidation of unsaturated hydrocarbons. The essential features of Bodenstein's mechanism are evident from the equations:



(A)

(B)

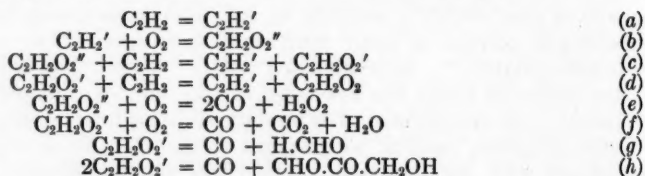
(C)

(D)

Molecule (C) is assumed to be formed from molecule (A) and molecule (D) from molecule (B). In this way there results, through the reproduction of molecule (C) (the active molecule produced in reaction (a)), a chain mechanism without any necessity for assuming a transfer of the energy of activation which has been the difficulty in mechanisms obtaining in liquid systems.

Bodenstein also applied this mechanism to the elucidation of the kinetics of acetylene oxidation as studied by Spence and Kistiakowsky<sup>27</sup> and found a satisfactory interpretation of the experimental results. More recent data have led Spence<sup>28</sup> to a slight modification of the suggested mechanism which satisfactorily accounts for the observed products which include carbon monoxide, carbon dioxide, glyoxal, formaldehyde, formic acid, and glycerosone, and also suggests a chain reaction with a chain length in wide vessels as long as 380. This latter was deduced from the influence of packing, which retards the rate of reaction, an influence first shown by Pease and Chesebro<sup>29</sup> for saturated hydrocarbons and by Hinshelwood and Thompson for hydrogen-oxygen explosions.<sup>30</sup> On the basis of chain mechanism the vessel walls terminate the chains which presumably involve radicals or atoms.

As amended by Spence, the Bodenstein mechanism is as follows:



The intermediate product is assumed to exist in two forms  $\text{C}_2\text{H}_2\text{O}_2''$  and  $\text{C}_2\text{H}_2\text{O}_2'$  which represent different energy levels in the glyoxal system and whose successive degradation to glyoxal introduces the possibility of branched chains, a necessity in explosive reactions. The formic acid arises from interaction of formaldehyde and hydrogen peroxide since both formaldehyde and formic acid are quite stable at the temperature of 325° C. used in these studies of acetylene oxidation.

Spence points out that the experiments of Lenher<sup>31</sup> on the slow oxidation of ethylene show a close parallelism to the acetylene results. The reaction has an

induction period, is strongly inhibited in packed vessels, and in open vessels the rate is determined by the nature of the wall. A feature of Lenher's experiments which indicates the close relationship which these reactions bear to the problem of preservation against deterioration is to be found in the fact noted by Lenher that polymerization of ethylene is much accelerated by the presence of small amounts of oxygen in the system. Oxidation of the hydrocarbon induces marked polymerization of the ethylene. This fact in itself is evidence of a chain mechanism for the process. It is paralleled by a number of analogous polymerizations which are induced by oxidation and are susceptible to the retarding influence of inhibitors.

**Polymerization as a Chain Reaction.**—The earliest researches of Moureu and Dufraisse<sup>32</sup> on the subject of prevention of deterioration were concerned with the stabilization of acrolein against polymerization. They found that this polymerization was greatly accelerated by traces of oxygen and also by exposure to light and that both processes were inhibited by a variety of substances, notably hydroquinone. These authors<sup>33</sup> showed that, even in absence of oxygen, light alone accelerated the formation of disacryl, shortening the reaction time from a year or more to a few seconds in strong sunshine. Furthermore, with such precautions against the absence of oxygen, hydroquinone increased the time of first observation of disacryl from 12 minutes (no hydroquinone) to more than 18 hours (1 per cent hydroquinone). These results indicate an accelerated polymerization by reason of an oxidation reaction, an association of reactions already emphasized by Engler and Weissberg<sup>34</sup> in their classical researches on autoxidation, but also the possibility of its initiation by light alone and the inhibition of the purely polymerization process by added agents.

Bäckström<sup>35</sup> in his experimental confirmation of the Christiansen chain reaction theory of inhibition cites these data of Moureu and Dufraisse as indicating that the polymerization reactions have chain characteristics similar to those of the autooxidation processes and that, in absence of oxygen, the inhibition process must involve "photochemical" reactions between active molecules of the reactant and the inhibitor. These side-reactions he described as "photochemical" because they involved energy-rich molecules which could be obtained either by reaction (including oxidation and polymerization) or by light absorption. It had already been pointed out by Taylor<sup>36</sup> that compound formation between reactant and inhibitor was often a characteristic of inhibited reactions and that an inhibitor acting in such manner would be particularly powerful since it would remove the active substrate molecules in competition with the oxygen, which is present only in very low concentration.

That such polymerization processes belong to the class of chain reactions is definitely indicated by the work of Starkweather and G. B. Taylor<sup>37</sup> on the kinetics of thermal polymerization of vinyl acetate alone or in solution and by the photochemical studies of H. S. Taylor and Vernon<sup>38</sup> on the polymerization of both vinyl acetate and styrene. In this latter work it was shown that a quantum of light energy was capable of producing the polymerization of as many as 1000 molecules of vinyl acetate. The polymerization of these vinyl compounds is enormously susceptible both to acceleration and retardation. Oxygen and peroxides are catalysts. Anti-oxidants such as sulfur, hydroquinone, etc., are powerful inhibitors. An extended study of comparative efficiencies of such inhibitors has recently been made by Alyea and Jeu<sup>39</sup> for the photo-polymerization of vinyl acetate. Hydroquinone, pyrocatechol, and especially pyrogallol have pronounced efficiencies. A comparison of the efficiencies thus obtained with those in sulfite oxidation suggests to Alyea and Jeu that the inhibitor is acting to stop an oxidation reaction, the assumption being made that the photo-polymerization of vinyl acetate requires the presence of a small amount of oxygen. Excess oxygen in the photo-polymerization of vinyl acetate

was shown by Taylor and Vernon to prevent polymerization. On the other hand, Conant and Peterson<sup>40</sup> have claimed that traces of peroxide are essential to polymerization of isoprene and *n*-butyraldehyde under pressure. As has been already mentioned it must, however, be borne in mind that the work of Moureu and Dufraisse with acrolein indicates a powerful photo-polymerization with careful regard to absence of oxygen in the system.

Alyea and Jeu have devised a new method of determining chain length based on their kinetic studies of rates of reaction for first order reactions in presence of inhibitors. Their general equation is:

$$\frac{2.3}{t} \log \frac{1}{1-x} = \frac{K}{k_2 + kC}$$

where  $x$  is the fraction reacting in time  $t$ ;  $K$  is composite of the number of chains initiated at  $t = 0$  and the probability of continuing the chains;  $k_2 + kC$  is the probability of breaking the chains by a constant factor  $k_2$  (wall or impurity), or by an inhibitor of concentration  $C$  and inhibitory power  $k$ . Alyea and Jeu show that a determination of the values of  $K$  and  $k_2$  permits a deduction of probable chain lengths from the values of  $k_2$ . In this way they find chain lengths in good agreement with the results of photochemical studies. For dilute solutions of vinyl acetate they find a polymerization chain length approximating 2500.

The polymerization of dienes is similarly sensitive to catalysts, light, and inhibitors, so that these cases may also be reckoned among the chain reactions. Butadiene and isoprene polymerize less readily than the vinyl compounds but they are sensitive to oxygen, ozonides, peroxides. It is of interest also to record that chloroprene,  $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$ , is sensitive in its polymerization<sup>41</sup> to similar catalysts, to light, pressure, and to inhibitors. In the presence of 1.6 per cent thiodiphenylamine and in presence of air the chloroprene was still fluid after 13 months in contrast to the 1 to 8 days required with peroxide or air alone as catalysts. Aromatic nitro compounds, notably trinitrobenzene, were notable members of the class of inhibitors for chloroprene. The formation of increased amounts of solid polymer, as an after-effect in the dark, after a preliminary illumination of the chloroprene vapor is the best possible evidence of a chain mechanism for this polymerization. The product is designated as the  $\omega$ -polymer and is regarded by Carothers as a cross-linked chain polymer.

**Chain Mechanism in Decomposition Processes.**—The outstanding example of a decomposition reaction for which a chain mechanism has been demonstrated is the decomposition of hydrogen peroxide solutions. The effect, as light screens, of added substances has already been emphasized but the greater efficiency of such substances when in the peroxide solution as compared with their effect when outside the peroxide has to be associated with the existence of a chain mechanism. Various substances, such as ethyl alcohol and ethylamine, sodium hydroxide, etc., which exert no influence as screens have nevertheless marked inhibitory powers even in minute concentrations on the photo-decomposition process. This is evidence, on the Christiansen theory, of a chain mechanism and a quantitative study of the reaction bears this out. Kornfeld<sup>42</sup> found that, in dilute solutions, up to 0.5 molar, the quantum yield, peroxide molecules decomposed per light quantum absorbed increased steadily to as much as 80 molecules/ $h\nu$ . The more comprehensive investigations of Allmand and Style<sup>43</sup> indicate even longer chains, dependent in length on the concentration of peroxide with a maximum between 1 and 2 moles per liter. The quantum yield in this region reached as high as 400 molecules per absorbed quantum at 21° C. varying with the wave length employed. Allmand and Style determined the temperature-coefficient of the reaction for three

wave lengths 3650, 3070, and 2750 Å. U. and found that the temperature coefficients were 1.42, 1.38, and 1.28 per 10° C., respectively, independent of peroxide concentration. This dependence of the temperature coefficient on wave length suggests a possibility of considerable interest to those interested in the discovery of chain reactions by photochemical studies. The decreasing temperature coefficient with increasing frequency strongly suggests that the temperature effect is concerned with the primary process. On a theory put forward by Tolman,<sup>44</sup> the activation energy calculated from such coefficients should represent the excess energy, over the average energy of all the molecules, required by an absorbing molecule in order that the absorption process shall initiate a reaction sequence. It was calculated by Allmand and Style that, on this assumption, with the coefficients observed, only a small fraction ( $<10^{-4}$ ) of all the absorbing molecules would react subsequent to absorption, and that, therefore, the chain length instead of being about  $10^2$  to  $10^3$  might actually be  $10^4$  to  $10^7$  links long. Such a chain length would be in good agreement with observed variations in the inhibitory powers of added substances as recently studied by Alyea and Jeu. They found that on the basis of pyrogallol as standard and equal to 3200 the inhibitory power of ethylamine was 20,300, phenol 11,300, hydroquinone 8400, ethyl alcohol 130, with acetamide only 33. Such varied inhibitory powers suggest chains  $10^4$  long or greater.

It might, therefore, be pertinent to offer this general observation. Quantum yields much greater than unity are definite photochemical evidence of the existence of chains. It may, however, arise that actual chain reactions show low quantum yields; in such circumstances only a fraction of the absorbed quanta initiate chains. As a corollary the quantum yield of the photo-process is a measure of the minimum chain length.

Allmand and Style showed that the decomposition of the peroxide solutions was, under certain conditions of concentration and wave length, proportional to the square root of the intensity of absorbed light. Such a relation to the light intensity is normally an index of the production of a photo-catalyst which subsequently disappears by a recombination process involving two of the species.<sup>45</sup> For this particular reaction Allmand and Style suggest two possible primary reactions:



or



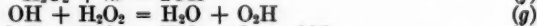
with the two possible recombination processes



or



Reaction (a) is the reaction process suggested by the nature of the absorption spectrum as studied by Urey, Dawsey, and Rice.<sup>46</sup> With such a primary process a chain mechanism similar to one suggested by Haber and Willstätter<sup>47</sup> for the decomposition of peroxide by the enzyme catalase. It may be formulated thus:



This latter reaction (h) may be better understood if written in two stages:



In the enzyme reaction Haber and Willstätter start the reaction chain at reaction (h) by the enzyme reaction:





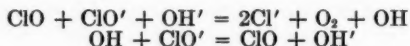
In both types of change the OH radical is the active link in the chains. The radical  $O_2H$  is a familiar radical in the intermediate stages of the hydrogen-oxygen reaction initiated by H atoms.<sup>48</sup> The chains would on this basis be ended by the reaction (c) above or by reaction of either  $HO_2$  or OH with the added inhibitor. In spite of much work already achieved with this simple process, much still remains to be accomplished before the problems of mechanism are finally solved.

With hypochlorites, the photochemical evidence for chains is not so positive. The best studies by Allmand and his colleagues<sup>49</sup> indicate quantum yield in the neighborhood of 1 to 3. There are certain results which do, however, indicate chains. The temperature coefficient of the  $Cl_2H_2O$  photolysis has a value of 1.4,<sup>50</sup> which at 20° higher temperatures than those employed by Allmand would give quantum yields considerably greater than 3, the maximum attainable without a chain mechanism. Further, for NaOCl solutions with a wave length of 2536 Å. U., Allmand and Webb found a value of 4.7 again in excess of the maximum non-chain possibility of 3.

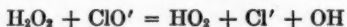
Quite recently Kauffmann<sup>51</sup> has cited chemical evidence pointing to a chain mechanism in hypochlorite decomposition. Bleach liquors may be activated by a variety of added agents such as hydrogen peroxide, hydrazine, ammonia, and formaldehyde. In the presence of such agents the bleach liquors show an enhanced oxidation activity toward dyes and other substrates such as cellulose. The discharge of the color of an Orange II dye which, with a given bleach liquor, may take 15 minutes, occurs practically instantaneously on addition of 1 ml. of 3-per-cent hydrogen peroxide to 100 ml. of the bleach liquor. That the action is not due to nascent oxygen from the peroxide is evident since hydrazine and ammonia act as activators. Kauffmann employs the Haber-Willstätter theory to provide a mechanism for the process, the first stage of which, as in the sulfite oxidation, consists in an ionic reaction producing a free radical:



In alkaline solutions a radical chain involving hydroxyl is thereby set up according to the equations:



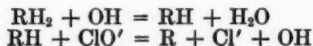
On this basis the activators are substances yielding hydroxyl in the liquid. Thus, with peroxide:



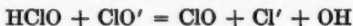
and possibly



The higher oxidation activity of the bleach liquors containing activators is associated by Kauffmann with the hydroxyl concentration thus produced and maintained by a chain mechanism, even in the oxidation of the substrate. Thus, if this latter be represented by the formula  $RH_2$  the following reaction chain sequence is possible:



In pure hypochlorites, containing no catalyst or activator, the reaction:



is a mechanism whereby the small activity of pure bleach liquors can arise. It is in agreement with this concept that the maximum activity of such liquors obtains at about  $p_H = 8$ , the equation indicating that both hypochlorite and ion are necessary to produce the reaction chain. Also the order of reaction for decomposition of

such liquors should be second order and dependent on alkali concentration—a fact known empirically for some years.<sup>52</sup>

### Applications

It will not be possible to present any extended development of applications of the principles already discussed. Such a presentation, if comprehensive, would occupy a volume in itself. Rather it is the aim in the succeeding paragraphs to indicate briefly, by particular examples, the practical importance of the fundamentals under discussion in such manner that application to other materials may be undertaken with adequate comprehension of the scientific factors involved.

**Rubber.**—The case of rubber is one in which conspicuous success has attended the application of the principles herein outlined. The aging of rubber, whereby it becomes hard and brittle, the development of cracks and loss of resistance to abrasion, the development, too, of stickiness in rubberized materials are all familiar phenomena. It is readily shown that the deterioration is due to the oxygen of the air, to light action or to both. The oxygen adds to the double bonds in the molecular structure and also promotes a decomposition of the rubber molecule, the latter continuing after the first is complete. The oxygen absorption curves are auto-accelerating in nature. During the course of the absorption the rubber first becomes tacky, then the tackiness disappears, and it becomes weak. Finally it becomes hard and brittle. The tackiness occurs at 80° C. after absorbing only 0.02 to 0.05 mole of oxygen per  $C_{10}H_{16}$  unit. After approximately 0.5 mole is absorbed the tackiness disappears and hardness and brittleness are reached after 1.0 mole is absorbed per  $C_{10}H_{16}$  unit. The tensile strength shows a tremendous change as a result of oxygen absorption. Absorption of oxygen equal to 0.5 per cent decreases the tensile strength by nearly 50 per cent, the diminution in strength being directly proportional to oxygen absorption over the range 0 to 1 per cent.

It is significant that the oxygen absorption is dependent on the curing process. The rate of oxygen absorption for raw rubber is less than that for cured rubber and increases with the degree of cure, facts in agreement with observations on the natural aging of cured rubber. Over-curing increases the rate of absorption of oxygen. It is certain, however, that the effect of oxygen on rubbers of different degrees of cure is not the same in all cases; the system is complex. The oxygen absorption and also the aging qualities of rubber are profoundly modified by incorporating in the rubber small amounts of chemicals known as antioxidants, anti-agers, or age-resistants. A wide variety of organic compounds is now in use for this purpose and has produced an important auxiliary chemical industry and a material improvement in the quality of rubber goods. Condensation products of aliphatic aldehydes and aromatic amines of various degrees of substitution are important members of this group of substances. It has been established that their influence is exercised on the rate of oxygen absorption; they materially reduce the rate of oxygen absorption, normally the more effectively the greater the concentration and dependent to a major degree on the constitution of the added inhibitor. They, therefore, behave analogously to the inhibitors of oxidation processes already discussed. The detailed interpretation of their action is naturally much more difficult than in the case of the simpler oxidizable compounds discussed in the theoretical portion of this work. There is evidence that raw rubber itself contains natural inhibitors of oxidation; hence the slow oxidation found with such material.<sup>53</sup>

As might be expected, deterioration is also sensitive to acceleration by catalysts and, as an example, the case of copper stearate may be cited. This substance is a vigorous accelerator of deterioration due to oxidation. Jones and Craig<sup>54</sup> show

that antioxidants bring about a retardation of deterioration in the presence of the copper accelerator roughly in the order of their efficiencies in absence of copper, the actual rates of deterioration being much greater, however, when copper was present than when absent. The presence of copper did not change the type of curve obtained with varying amounts of the inhibitor phenyl- $\beta$ -naphthylamine, which, in presence and absence of copper, did not markedly influence the rate of deterioration when present in concentrations beyond about 1 per cent inhibitor. The research shows that the catalyst and inhibitor each exercises its normal functions and that together they tend to neutralize the effect due to each. The possible catalytic effects of added materials is a matter of importance in the choice of pigments to be compounded with rubber.

Experience shows also the importance of light in this case. It undoubtedly speeds up the reactions involved.<sup>55</sup>

**Hydrocarbons.**—The problem of deterioration in respect to hydrocarbons includes the keeping qualities of gasoline and transformer oils. In the former case the problem has recently become more acute by reason of the greater production of cracked gasolines with a relatively high concentration of unsaturates with special emphasis on the presence of diolefines. The tendency to gum formation in gasolines is due mainly to the diolefines although the simple ethylenes may form gum on extended oxidation. Kogerman<sup>56</sup> showed recently that 2,4,hexa- and pentadienes absorb 2 moles of oxygen per pair of double bonds yielding compounds similar to the gums obtained in cracked gasoline. It is well known that absorption of oxygen is a preliminary stage in the development of gumminess in such gasolines and the rate of absorption is of the now-familiar auto-accelerative type accompanied by the accumulation of peroxides. There is a preliminary induction period during which, undoubtedly, inhibitors, probably of a phenolic nature, present in the natural materials, are performing their function as retarding agents. Peroxides added initially to the gasoline eliminate the induction period presumably through oxidation of the inhibitors. The natural inhibitors may be removed by alkali washes whereupon, again, the induction period is shortened. The interaction of added peroxides with inhibitors, destroying these latter, is not without its important practical significance in the technique of inhibitor addition. It suggests that, for maximum inhibitor efficiency, the gasolines to which they are added should be as substantially free from peroxides as practical. Otherwise the inhibitors will be readily removed by oxidation and their retardation efficiency destroyed. The high temperatures of cracking distillations are generally sufficient to decompose any peroxides present so that a freshly distilled cracked gasoline should be substantially free from peroxides. It is at such a stage that maximum inhibitor efficiency may be obtained. The lower temperatures of straight distillation may not be high enough to decompose peroxides which may, therefore, be carried over.\* These should be removed prior to inhibitor addition for maximum efficiency of the latter.

There is definite evidence<sup>57</sup> that most, if not all, of the residue left when gummy gasoline is evaporated is formed from peroxides during the evaporation. It is this fact that makes the problem of gum prevention a problem of inhibition of oxidation. Of inhibitors a large patent literature exists, as examples of which the following may be cited: hydroquinone, anthracene, acetanilide, phenol, methylaminophenol, and the corresponding benzyl derivative.

Refined transformer oil is mainly composed of saturated hydrocarbons with a less tendency to oxidation than oils containing unsaturated hydrocarbons capable of forming peroxides. Nevertheless, oxidation of the saturated hydrocarbons does occur even at ordinary temperatures and this oxidation is greatly accelerated by

catalytic materials. Copper, iron, lead, manganese, and cobalt soaps are powerful accelerants of such oxidations. Preservation of these oils from deterioration resolves itself in part, therefore, into attempts to keep the concentration of such accelerants down to a minimum. With the metal containers and equipment necessary in the use of such oils, attention must, therefore, be paid to the presence of acidic constituents in the oil, since these will attack metals and their oxides yielding the accelerant soaps. Quite recently the use of selenium and sulfur in such oils as well as organic sulfides such as isoamyl sulfide has been shown to diminish the oxidation of transformer oils.<sup>58</sup> More sludge is formed with sulfur in the oil than without, and these authors indicate that heavy sludge-forming oils contain certain amounts of sulfur and unsaturated compounds, both necessary for sludge formation in their view.

It is known that light accelerates the decomposition processes occurring in such oils. Also, the effect of the electric fields present in such oils in use is an item of importance in their stability. As is well known, these fields produce decomposition of hydrocarbons into fragments which then have further possibilities of reaction. It is these latter reactions in which the possibility of a chain mechanism most prominently arises and against which the utilization of inhibitors may be invoked. A number of patent applications is concerned with the stabilization of transformer oils against the action of air, light, and electrical action. Hydroxybiphenyls have been proposed for such purposes.<sup>59</sup>

The development of antiknock gasolines is in reality the prevention, by blending of suitable hydrocarbon mixtures or by addition of suitable antioxidant materials, of a premature deterioration of hydrocarbons under the temperature-pressure conditions obtaining in the internal combustion engine. The reactions occurring are characteristically chain reactions. An extended treatment of this familiar field is impossible in the present survey.

**Fats and Oils.**—Observations of suppression of rancidity and oxidation of oils date back well into the first half of the nineteenth century. Moureu and Dufraisse call attention to the observation of Deschamps in 1843 that fresh lard containing gum benzoin or populin did not become rancid as did pure lard. Moureu and Dufraisse attribute this to the antioxygenic activity of the benzoin and saligenin contents of the added agents. Oak wood was shown by Chevreul in 1856 to inhibit the drying of linseed oil; poplar and pine wood showed the same phenomenon in less degree. Moureu and Dufraisse ascribe this to the presence of tannin in the woods. They themselves included linseed oil, nut oil, and butter in the list of substances for which they demonstrated the effect of inhibition of oxidation. The phenomenon is, therefore, of importance in the field of paints and varnish, in the artificial leather industry (nitrocellulose-castor oil films), in the field of pharmaceuticals (cod-liver oil), and in the edible oil industry (beef fat, butter, lard).

The drying of oils is, in large part, an oxidation process very sensitive to positive catalysts (driers, lead, cobalt, manganese soaps, etc.) and to the accelerating action of light. Oxygen is absorbed at rates auto-accelerative in nature, the induction period being a function of the amount of accelerators present and dependent, in the absence of these, on the amount of natural inhibitors present. A variety of antioxidants prolong the induction period greatly. It is evident that these antioxidants are consumed in minimizing oxidation of the oil, for, after an induction period due to added inhibitors, the rate of oxygen absorption is substantially what it would have been without the intervening induction period. It was shown by Rogers and Taylor<sup>60</sup> that the drier and inhibitor apparently act independently of each other in a manner consistent with the view that the drier starts reaction chains and the inhibitor breaks chains, itself being oxidized. Consistent with such oxidation of



the inhibitor are also the observations of Wagner and Brier<sup>61</sup> that inhibitor added after the termination of the induction period at 100° C. is not effective as an anti-oxidant. At 30° C. it is effective in inverse ratio to the rate of oxidation. Both facts point to a removal of inhibitor by oxidation due to accumulation of peroxide in the oxidizing material. The addition of partially oxidized linseed oil to a system which normally undergoes an induction period shortens the induction period to an extent directly proportional to the amount of addition, a fact also pointing to consumption of inhibitor.

The utilization of inhibitors for the protection of paint and varnish films thus stumbles on the difficulty that the process which produces the film is retarded by materials which might be added to the mixture to protect against subsequent deterioration the films produced; and also the drying process itself destroys such added preservatives. Hence it would seem that the only available possibility in the case of paints and varnishes is that proposed by Scheiber,<sup>62</sup> of applying to a finished coat of paint an additional coat of inhibitor dissolved in a suitable solvent which would permeate to a degree the paint vehicle. In paints of the nitrocellulose type which do not involve a "drying" process, but only solvent evaporation, a wider scope for the use of inhibitors is possible.

Since many pigments are accelerative of oxidation processes, a positive control of deterioration in paints and varnishes can be obtained by due attention to the pigments used. Especial care should be exercised to see that, so far as possible, inert, non-oxidative pigments are employed. A material improvement in paint film life can thereby often be secured.

With compositions containing non-drying oils, which are, however, subject to oxidation processes, a more positive effect can be secured from the use of inhibitors. Thus, as shown by Rigakusi,<sup>63</sup> the oxidation of castor oil is markedly diminished by the presence of such agents as diphenylhydrazine and  $\alpha$ -naphthylamine. One may, therefore, expect beneficial effects from such materials in nitrocellulose-castor oil films present in artificial leather and consequent protection of such against the aging common to such materials. Also, with such materials, the absence of oxidative pigments is also desirable in the interests of durability.

Light, heat, and inorganic salts such as those of copper are powerful accelerants of the oxidation of butter and lard.<sup>64</sup> The effect of gum benzoin and saligenin as inhibitors of such oxidation has already been mentioned. Vibrans<sup>65</sup> has recently indicated that 0.5 per cent of diphenyl ethylenediamine or 0.2 per cent of thymol are preventives of rancidity in vegetable oils. Similar considerations apply to pharmaceuticals such as cod-liver oil.

**Ethers and Essential Oils.**—It has long been known that ethers formed peroxidic products in contact with air and that light and catalysts accelerated the oxidation process. Milas<sup>66</sup> has recently shown that in addition to the accelerative action of light and metals there is an inhibitory action by such substances as iodine, picric acid, and benzoquinone. Delepine<sup>67</sup> had earlier shown that a variety of thioethers oxidize with accompanying chemiluminescent effects (a criterion, according to Bäckström, of a chain mechanism) and that ether, ethylene oxide, turpentine, ethyl and methyl alcohols, benzene, etc., diminish the oxidation process.

Milas<sup>68</sup> has also made extended studies of autooxidation phenomena, inhibited by added agents, with a variety of essential oils.

**Textiles and Cellulose.**—Sisley and Seyewetz<sup>69</sup> have claimed the protection of silk against light, heat, and atmospheric action by means of thiourea, hydroquinone, and their derivatives. Similar studies with other textiles would be advantageous. Dye-stuffs such as azo-dyes and eosin are apparently protected against light action by inhibitors. The deterioration of textiles and paper by aging and by



light action is well known although the importance of the various factors involved has not been decisively settled. Undoubtedly, attention should be paid to the effects of inorganic constituents, such as alkalis and iron compounds, present in the ash since it is known that such agents have enormously positive accelerating effects on the autooxidation of analogous compounds such as the polyhydroxy alcohols.<sup>70</sup> The oxidation of such materials also by reagents employed in bleaching processes is also pertinent to the problem on hand.<sup>71</sup>

Enough has been cited by way of exemplification to show that the problem of deterioration in a wide variety of important products is one to which the fundamentals laid down in the preceding sections are eminently applicable and, therefore, warrants, by those concerned, a systematic and scientific investigation for eventual solution.

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# The Elastic Behavior of Vulcanized Rubber

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Up to extensions of about 270 per cent the elastic behavior of vulcanized rubber can be represented analytically by a very simple function. The stress-strain diagrams for tension and compression are quite different; nevertheless this asymmetrical behavior is satisfactorily taken care of by employing only two elastic coefficients.

The mental attitude of the engineer to an organic compound such as rubber is a very skeptical one if its elastic behavior has to be compared with that of metals; nevertheless experiments with rubber belts furnished by the Goodyear Tire and Rubber Company to the Massachusetts Institute of Technology have convinced the author of this paper that a comparison of the elastic properties of rubber with those of metals is justified and at the same time very instructive as regards the mechanics of finite deformations in general.

Naturally rubber is more easily influenced by temperature and by surrounding liquid and gaseous substances which eventually cause chemical changes. However, vulcanized rubber can now be manufactured of such excellent quality that the way is opened to uses hitherto not exploited. Of these may be mentioned the use of rubber tires for the wheels of steam locomotives, enabling the latter to climb steep grades, and the wide field of application on damping vibrations and changing unfavorable critical speeds, already exemplified in the automotive industry.

Such applications can only be industrially exploited if the elastic stresses in rubber obey a known, mathematically defined law. In this paper the author therefore develops the law for large deformations and shows its agreement with the results of experiments made with the two rubber compounds that were furnished.

## General Law of the Ideal Elastic Body

We call a material ideally elastic if, even after a considerable deformation, it assumes its original shape after removal of the constraints introduced and if the process of loading and unloading is not accompanied by transformations of mechanical energy into heat (cf. *J. Rheology*, 2, No. 2, 169). Nearly all materials are ideally elastic if the deformation is infinitesimal, but in the case of most substances finite deformations are accompanied by losses of mechanical energy. It is not the aim of this paper to study these losses, but it may be mentioned that there is even in the realm of ideal elasticity an unexplored region indicated by the experimental fact that the law for infinitesimal elastic deformations does not hold good for finite deformations. It is only necessary to subject a rubber cylinder to tension and compression at comparatively small strains, when the lack of agreement becomes obvious.

At the foundation of all elastic theories lies the definition of strain, and before introducing a new law of elasticity we must explain how finite strain is to be measured.

Infinitesimal strain is measured by the ratio of the increase in length to the length

itself. In defining a considerable strain  $\lambda$  of a fiber we assume this strain to be divided into small portions  $d\lambda$ . Each of these portions we define, as in the case of an infinitesimal strain, by the ratio:

$$d\lambda = \frac{dx}{x} \quad (1)$$

where  $x$  is the length of a fiber in a certain state of strain. Integrating and taking the length of the fiber before stressing as  $a$  and after stressing as  $b$ , we get

$$\lambda = \log_e \frac{b}{a} \quad (1a)$$

Our measure of finite strain is therefore the natural logarithm of the ratio of the two lengths.

On the basis of the general theory developed in the Appendix we obtain the law of the simple *uniaxial* tension and compression test of rubber in the following two forms:

*Stress per Unit Area Referred to the Deformed State:*

$$\sigma = 2G\lambda \left( e^\lambda + \frac{1}{2} e^{-\lambda/2} \right) \quad (2a)$$

*Stress per Unit Area Referred to the Undeformed State:*

$$\sigma_0 = 2G\lambda \left( 1 + \frac{1}{2} e^{-3\lambda/2} \right) \quad (2b)$$

If  $P$  is the load,  $A_0$  the area of cross section of the unloaded specimen, and  $A$  the area after the load is applied, we have, for incompressible material,  $A = A_0 e^{-\lambda}$ . The stress  $\sigma_0$  is the observed stress, because all testing machines measure directly the force applied and not the true physical stress  $\sigma$ .

The coefficient  $G$  is about 67 lb. per sq. in. for the material examined and is the same as the modulus of shear for infinitesimal deformations. For such deformations both Equations (2a) and (2b) yield

$$\sigma = \sigma_0 = 3G\lambda$$

On the basis of Equations (2a) and (2b) and taking  $2G = 134$  lb. per sq. in., Table I has been calculated and the values plotted in Fig. 1.

TABLE I

$+\lambda$	$e^\lambda + \frac{1}{2} e^{-\lambda/2}$	$\lambda(e^\lambda + \frac{1}{2} e^{-\lambda/2})$	$\sigma$	$\sigma_0$
0.0	1.500	0.0	0	8
0.2	1.674	0.3348	45	37
0.4	1.901	0.7604	102	60
0.6	2.192	1.3152	176	97
0.8	2.561	2.0488	275	124
1.0	3.021	3.021	405	149
1.2	3.594	4.32	580	174
1.4	4.303	6.03	810	200
1.6	5.178	8.29	1110	224

An analogous table for the negative values of  $\lambda$  is given in Table II.

TABLE II

$-\lambda$	$e^{-\lambda} + \frac{1}{2} e^{\lambda/2}$	$\lambda(e^{-\lambda} + \frac{1}{2} e^{\lambda/2})$	$\sigma$	$\sigma_0$
0.0	1.500	0.0	0	0
0.2	1.371	0.2742	37	45
0.4	1.281	0.5124	69	102
0.6	1.224	0.7344	98	179
0.8	1.195	0.9560	128	285
1.0	1.192	1.192	160	435
1.2	1.212	1.455	195	645
1.4	1.253	1.750	235	951
1.6	1.315	2.100	282	1397

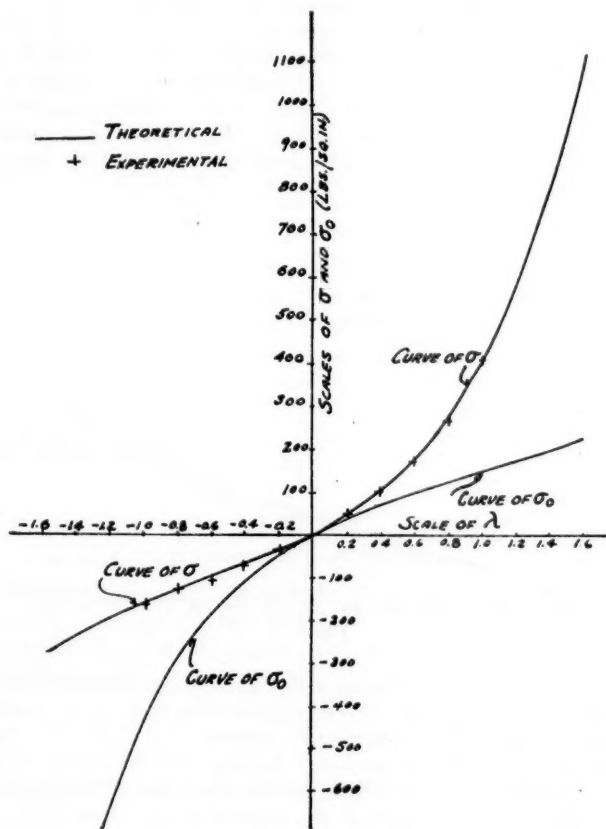


Figure 1

### Experiments

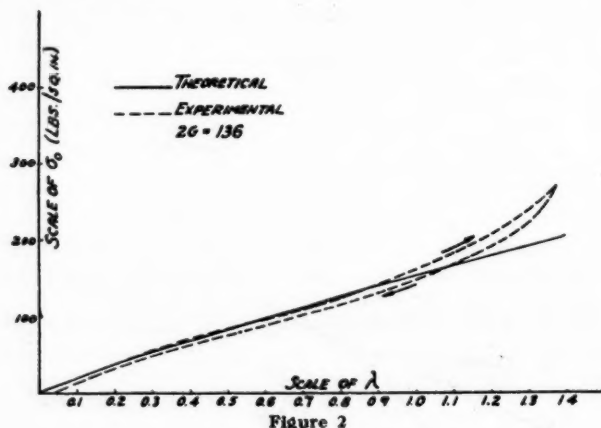
The rubber with which the experiments were made was delivered in form of closed belts of 2 in.  $\times$  0.32 in. cross section and 38 in. circumference. Two different compounds (Nos. 4183 and 4799) were used and there were 12 belts in all. The values of the elastic constants are about the same for both compounds, but slight variations in the elastic constants occur even at different parts of one and the same specimen.



*The Bulk Modulus.*—To measure the bulk modulus, rubber cylinders 1 in. in diameter and 1.5 in. long were placed in a compression chamber and the distance between the pressure heads measured with Ames dials. The bulk modulus  $K$  was found to be 387,000 lb. per sq. in. or 27,200 kg. per sq. cm. (average of three experiments). This is somewhat larger than the modulus of water, which is 23,000 kg. per sq. cm., but agrees well with the fact that the specific gravity of rubber is about the same as that of water.

Considering the great difference between the shear and bulk moduli (their ratio is  $G/K = 0.211 \times 10^{-3}$ ), it is justifiable to consider rubber as incompressible in the range for which validity is claimed for the elastic law (2). The commonly used modulus of elasticity  $E$  is in that case equal to  $3G = 200$  lb. per sq. in.

*The Tensile Test.*—The tensile test under uniaxial stress is technically very easy to carry out. However, by an increase in length of 200 per cent or more, time effects and elastic strain hardening play an important role. The strain hardening is due to the microstructure of rubber and can only be taken into account by employing a statistical theory. This strain hardening has in some respects the character of internal friction; therefore the unloading curve coincides nearly with the author's theoretical curve.



The curves of Fig. 2 show the loading and unloading at a constant rate of applying strain and removing stress (time of loading and unloading, 4 hrs. in all) with the stresses related to the original area of cross section. Table III gives the values of the true stresses and strains for very slow loading and unloading. The observed values of  $\lambda$  are reduced to equal differences by interpolation, because it would not have been possible otherwise to take the average of the experiments with three specimens.

TABLE III  
Calculated Stress  $\sigma$   
(Equation [2a]),  
Lb. per Sq. In.

+  $\lambda$   
0.0  
0.2  
0.4  
0.6  
0.8  
1.0

Measured Stress  $\sigma$ ,  
Lb. per Sq. In.

0.0  
44.5  
100.7  
171.0  
270.8  
410.0

*The Compression Test.*—The compression test is very difficult to perform and almost impossible to carry out for higher pressures if uniaxial stress has to be used. Not only is the state of uniform uniaxial stress unstable even for comparatively short rubber cylinders, but it is even difficult to realize such a state of stress. Despite careful greasing of the planes of contact with the pressure heads of the testing machine, dry friction was detected. Evidently the grease is removed under too much pressure. Table IV gives the calculated and measured stresses.

TABLE IV  
Calculated Stress  $\sigma$   
(Equation (2a)),  
Lb. per Sq. In.

$-\lambda$	Calculated Stress $\sigma$ (Equation (2a)), Lb. per Sq. In.	Measured Stress $\sigma$ , Lb. per Sq. In.
0.0	0.0	0.0
0.2	36.8	37.3
0.4	68.7	72.7
0.6	98.5	103.7
0.8	128.0	129.8
1.0	160.0	162.4

The change in the elastic behavior in going from positive to negative strains is very marked, but is satisfactorily represented by the theoretical formula. Figure 2 shows the deviations from the theoretical curve at the larger strains.

### Conclusions

As a consequence of the work described the author arrives at the conclusion that in the deformation range from 0 to 270 per cent only one elastic constant is needed for a full mathematical description, and that this constant is the modulus of shear defined for infinitely small deformations.

If models could be made of rubber at less expense, this material could be used for the integration of the equations of elasticity. The solutions could be easily corrected for the lack of compressibility and for the change in the common law of elasticity.

### APPENDIX

#### Mathematical Derivations

Taking an element of a body and stressing it in three directions perpendicular to each other,  $x_1, x_2, x_3$ , we get the new lengths  $\overline{dx_1}, \overline{dx_2}, \overline{dx_3}$  from the old ones  $dx_1, dx_2, dx_3$ . If we denote the principal strains by  $\epsilon_1, \epsilon_2, \epsilon_3$ , the corresponding strains are, according to (1) and (1a),

$$\epsilon_1 = \log_e \left( \frac{\overline{dx_1}}{dx_1} \right) \quad (3)$$

It is very convenient to take the average of these strains, namely,

$$\epsilon = \frac{1}{3} (\epsilon_1 + \epsilon_2 + \epsilon_3) \quad (3a)$$

whence

$$3\epsilon = \log_e \left( \frac{\overline{dx_1} \overline{dx_2} \overline{dx_3}}{dx_1 dx_2 dx_3} \right) = \log_e \left( \frac{dV}{V} \right)$$

$\epsilon$  arises from that part of the strain which is equal in all directions. Consequently if we subtract  $\epsilon$  from  $\epsilon_1, \epsilon_2, \epsilon_3$ , and denote the result by  $\varphi_1, \varphi_2, \varphi_3$ ,

$$\varphi = \epsilon_1 - \epsilon \quad (3b)$$

will represent the pure deformation without the change in volume. We can resolve the stresses acting at any point in the same manner.  $S = 1/3 (S_1 + S_2 + S_3)$  is that part of the stress which can exist in an ideal liquid. This hydrostatic part of the stress  $S$  is connected with the change of volume, the remainder of the stress,  $S_1 - S$ , is connected with the change of form.

Now in the case of infinitely small strains it is not necessary to state that the stresses in the deformed states are to be employed when we formulate the elastic law. It does not make any difference for which state we give the stresses. With finite deformations, however, only the true physical stresses after equilibrium is attained can be used. For any homogeneous and isotropic material we can write down easily the simplest form the elastic energy can assume. We introduce into this two moduli, the modulus of shear  $G$  and the bulk modulus  $K$ , and choose the simplest possible analytical form, which becomes the expression of the classical theory of elasticity when we assume infinitely small displacements:

$$2W = 2G (\varphi_1^2 + \varphi_2^2 + \varphi_3^2) + 9K\epsilon^2 \quad (4)$$

$W$  is the elastic energy per unit volume in the undeformed state. The energy must be related to the undeformed state because it is a physical entity connected with the mass of the body. Equation (4) is naturally an assumption and has to be checked by experiment.

But there is yet another doubt. Must we not relate the formula for the energy to the real bearer of the energy, the molecule? If the substance is built up from such units, should we not assume expression (4) as the energy of the molecule? Our experimental results indeed point in this direction. But before we study this question we shall formulate another expression for the work done which is independent of any law of elasticity.

If  $dV$  is the volume before and  $\overline{dV}$  the volume after the deformation,

$$\delta W dV = S_1 \overline{dx_2} \overline{dx_3} \delta \overline{dx_1} + S_2 \overline{dx_1} \overline{dx_3} \delta \overline{dx_2} + S_3 \overline{dx_1} \overline{dx_2} \delta \overline{dx_3}$$

or

$$\delta W = \frac{\overline{dV}}{dV} (S_1 \delta \epsilon_1 + S_2 \delta \epsilon_2 + S_3 \delta \epsilon_3) = e^{3\epsilon} (S_1 \delta \epsilon_1 + S_2 \delta \epsilon_2 + S_3 \delta \epsilon_3) \quad (5)$$

$e^{3\epsilon}$  is the relative volume, and will be denoted by  $v$ . Assuming now that Equation (4) is applied to isotropic and continuous matter, we can immediately derive the law of elasticity.

By differentiating [4],

$$\begin{aligned} \delta W &= 2G[\varphi_1 (\delta \epsilon_1 - \delta \epsilon) + \varphi_2 (\delta \epsilon_2 - \delta \epsilon) + \varphi_3 (\delta \epsilon_3 - \delta \epsilon)] + 3K\epsilon (\delta \epsilon_1 + \delta \epsilon_2 + \delta \epsilon_3) \\ &= \delta \epsilon_1 (2G\varphi_1 + 3K\epsilon) + \delta \epsilon_2 (2G\varphi_2 + 3K\epsilon) + \delta \epsilon_3 (2G\varphi_3 + 3K\epsilon) \end{aligned}$$

Comparing this expression with Equation (5),

$$S_1 v = 2G\varphi_1 + 3K\epsilon \quad (6a)$$

or in another form,

$$\left. \begin{aligned} S_1 - S &= \frac{2G}{v} \varphi_1 \\ S &= \frac{K}{v} \log_e v \end{aligned} \right\} \quad (6b)$$

The apparent increase of the modulus of shear for high compression measured by Bridgman is accounted for in Equation (6b), because  $\nu$  is in that case less than unity.

For rubber  $\nu$  differs but little from unity so long as  $S$  is in the range of 0–4000 lb. per sq. in.

Under these circumstances we can neglect the change in volume entirely, writing

$$S_1 = 2G\varphi_1 + S \quad (7)$$

for an ideal incompressible material.

But having considered an element  $dx_1, dx_2, dx_3$  of continuous matter which led us to Equation (7), we now assume an element containing thousands of molecules. As it does not matter which form we assume them to be in, let us take them as small spheres. The true shape of the molecule of rubber is not known, but it probably is of a prismatic form. We must keep clearly in mind, therefore, that we are neglecting the true microstructure of rubber in assuming spherical molecules.

Here we no longer apply Equation (7) to the stresses, but to the forces with which the molecules act on one another, writing

$$P_1 - P = 2G'\varphi_1 \quad (8)$$

where  $P = \frac{1}{3}(P_1 + P_2 + P_3)$ .

If  $N$  is the number of molecules lying in the unit of area of a certain cross section in the undeformed state, then after deformation there will be in the  $dx_2, dx_3$  plane the number  $Ne^{\varphi_1}$  molecules since

$$\frac{\overline{dx_2}}{dx_2} \frac{\overline{dx_3}}{dx_3} = \frac{\overline{dx_1}}{dx_1} = e^{-\varphi_1}$$

for  $\epsilon = 0$ .

Multiplying Equation (8) by  $Ne^{\varphi_1}$  gives the true stresses

$$Ne^{\varphi_1}(P_1 - P) = 2G'N\varphi_1e^{\varphi_1}$$

$$Ne^{\varphi_2}(P_2 - P) = 2G'N\varphi_2e^{\varphi_2}$$

$$Ne^{\varphi_3}(P_3 - P) = 2G'N\varphi_3e^{\varphi_3}$$

These stresses now comprise an amount of hydrostatic stress which has to be subtracted. As the hydrostatic stresses in incompressible material are not elastically but statically determined, we can so determine them and, putting  $G'N = G$ , obtain

$$S_1 - S = 2G \left[ \varphi_1 e^{\varphi_1} - \left( \frac{\varphi_1 e^{\varphi_1} + \varphi_2 e^{\varphi_2} + \varphi_3 e^{\varphi_3}}{3} \right) \right] \quad (9)$$

Putting  $\varphi_1 = \lambda$ ,  $\varphi_2 = \varphi_3 = -\frac{1}{2}\lambda$ ,  $S_1 = \sigma$ , and  $S = \frac{1}{3}\sigma$  in (9) we get Equation (2a), and then, after dividing by  $e^\lambda$ , Equation (2b).

It is easy to generalize the law (9) so that it can be applied to other substances. We wish, however, to conserve under all circumstances the condition that the stresses can be derived from an elastic potential.

If we put

$$\left. \begin{aligned} S_1 - S &= \frac{2G}{\nu} \left\{ f(\varphi_1) - \frac{1}{3} [f(\varphi_1) + f(\varphi_2) + f(\varphi_3)] \right\} \\ S &= \frac{3K}{\nu} \psi(\epsilon) \end{aligned} \right\} \quad (10)$$

the work done by the stresses, with  $\epsilon_1 = \epsilon + \varphi_1$ ,  $\epsilon_2 = \epsilon + \varphi_2$ ,  $\epsilon_3 = \epsilon + \varphi_3$ , will be, according to (5),

$$\delta W = [(S_1 - S)\delta\varphi_1 + (S_2 - S)\delta\varphi_2 + (S_3 - S)\delta\varphi_3 + 3S\delta\epsilon]v$$

Introducing the value of  $S_1 - S$  from (10),

$$W = 2G \left[ \int_0^{\varphi_1} f(\varphi_1)\delta\varphi_1 + \int_0^{\varphi_2} f(\varphi_2)\delta\varphi_2 + \int_0^{\varphi_3} f(\varphi_3)\delta\varphi_3 \right] + 9K \int_0^{\epsilon} \psi(\epsilon)\delta\epsilon \quad (11)$$

The functions  $f(\varphi_i)$  and  $\psi(\epsilon)$  must therefore be obtained experimentally.

The use of Equation (11) is more satisfactory than that of expressions which can be considered only as interpolation formulas of the experiments, because, according to (11), the work done is independent of the manner in which the material is loaded.

In the study of the behavior of rubber under deformations greater than 270 per cent we cannot neglect the influences of the time effects comprising relaxation and creeping (see Fig. 2). The shape of the rubber molecules also plays an important part in the behavior under very large deformation.

The study of these deformations is not important for technical purposes because in practice such large strains are never used, but the subject is very interesting from the standpoint of physical chemistry, because it enables definite conclusions to be drawn concerning the microstructure of rubber.

#### Acknowledgments

Grateful acknowledgment is due to Prof. H. W. Hayward of the Massachusetts Institute of Technology for valuable aid and support, to the Goodyear Tire and Rubber Co. for furnishing the specimens, and to I. Silverman for his assistance in carrying out the tests.



# Heat Treatment of Vulcanized Rubber

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## Introduction

The fundamental process in rubber reclamation is a heat treatment at about 160° C. for several hours. The molecules of the vulcanized rubber are thereby depolymerized and their original properties are restored to such an extent that the product may be substituted in part for raw rubber in formulas for new goods. Although the principal cause of the aging of rubber is considered to be oxidation, the effects of heat developed by friction in the use of products such as rubber belting and tires cannot be disregarded. The usual methods of chemical analysis may be applied to the study of rubber samples vulcanized by heating, and information so gained may throw some light on the complex phenomena of the aging and reclamation of rubber.

## Experimental Procedure

A simple mixture of 93 per cent pale crepe and 7 per cent (by weight) of acid-free sulfur was used. This was milled for 12 minutes and mixed for 13 minutes by passing between the heated rollers. Test samples were vulcanized for 20-, 40-, 60-, 80-, and 100-minute periods at 60 lbs. per sq. in. steam pressure. As indicated by data in Table I, the optimum time of vulcanization for the best mechanical strength was 80 minutes.

TABLE I

Time of vulcanization (min.)	20	40	60	80	100
Tensile strength (kg. per sq. cm.)	95	130	139	148	31
Elongation (percentage)	994	974	931	841	571

The sheets of vulcanized samples were passed between rollers and milled sufficiently to pass a 14-mesh sieve. Powdered samples thus prepared were placed in beakers and heated on an oil bath at 160° C. for 0.5-, 1.0-, 1.5-, 2.0-, 3.0-, and 4.0-hour periods. The beakers were covered with watch glasses and the contents stirred occasionally. It was noticed that some viscous material and sulfur were condensed on the watch-glass during the heating. The samples became viscous at first, but this tendency disappeared after 3 or 4 hours, small brittle masses remaining.

Acetone and chloroform extracts, free and total sulfur were then determined. Combined sulfur and resins were calculated by difference. Changes in weight of samples resulting from the heating were noted.

## Changes in Acetone Extract

The results of the 8-hour extractions with acetone in the Cottrell apparatus are given in Table II, and in Fig. 1.

TABLE II

		Duration of Heating (Hours)						
		0	0.5	1.0	1.5	2.0	3.0	4.0
A	Acetone ext. (%)	8.35	13.19	19.38	17.54	16.05	11.72	10.15
	Ratio	1.00	1.58	2.32	2.10	1.92	1.40	1.22
B	Acetone ext. (%)	8.57	18.68	15.34	15.17	13.57	10.15	7.71
	Ratio	1.00	2.18	1.79	1.77	1.58	1.18	0.90
C	Acetone ext. (%)	6.23	17.36	22.11	15.73	13.08	8.58	6.75
	Ratio	1.00	2.79	3.55	2.52	2.10	1.39	1.09
D	Acetone ext. (%)	4.47	22.56	19.92	15.73	13.32	8.09	7.04
	Ratio	1.00	5.05	4.46	3.52	1.81	1.57	1.57
E	Acetone ext. (%)	4.93	21.60	19.34	16.86	14.28	9.72	7.05
	Ratio	1.00	4.38	3.92	3.42	2.89	1.97	1.43

A, B, C, D, and E are the samples vulcanized for 20, 40, 60, 80, and 100 minutes, respectively.

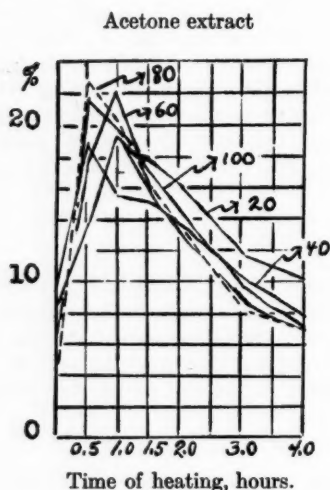


Figure 1

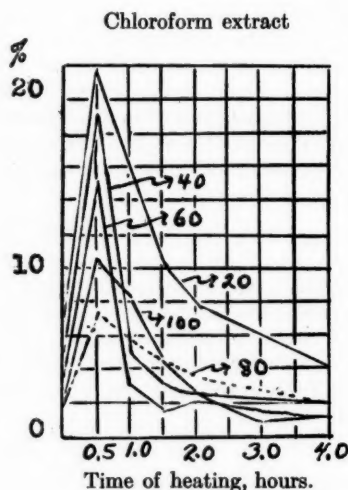


Figure 2

### Change in Chloroform Extract

The results of the 20-hour chloroform extractions of the acetone-extracted samples are given in Table III and Fig. 2.

TABLE III

		Duration of Heating (Hours)						
		0	0.5	1.0	1.5	2.0	3.0	4.0
A	CHCl <sub>3</sub> ext. (%)	6.95	21.81	16.23	10.21	7.81	6.03	4.24
	Ratio	1.00	3.13	2.33	1.44	1.12	0.87	0.61
B	CHCl <sub>3</sub> ext. (%)	5.36	19.34	4.82	3.00	2.55	2.20	1.85
	Ratio	1.00	3.61	0.90	0.56	0.48	0.41	0.35
C	CHCl <sub>3</sub> ext. (%)	3.38	15.02	3.03	1.52	2.07	1.58	1.16
	Ratio	1.00	3.94	0.79	0.40	0.54	0.41	0.30
D	CHCl <sub>3</sub> ext. (%)	1.67	7.36	5.63	4.66	3.54	2.81	1.81
	Ratio	1.00	4.41	3.37	2.79	2.12	1.68	1.08
E	CHCl <sub>3</sub> ext. (%)	2.27	10.64	8.34	4.38	2.65	0.89	1.17
	Ratio	1.00	4.69	3.66	1.93	1.17	0.39	0.52

A, B, C, D, and E are the samples vulcanized for 20, 40, 60, 80, and 100 minutes, respectively.

### Changes in Free, Total and Combined Sulfur, and Resinous Substance

These are indicated in Table IV and Figs. 3-6. The free sulfur was determined by oxidizing the acetone extract with bromine and nitric acid.

### Changes in Weight of Samples

The changes in weight of the samples were estimated by placing one-gram samples in weighing flasks and heating in beakers in an oil bath. The results are shown in Table V and Fig. 7.

The changes in acetone and chloroform extracts of the raw rubber on heating were determined as with the vulcanized rubbers after it was milled for 25 minutes. The results are shown in Table VI.

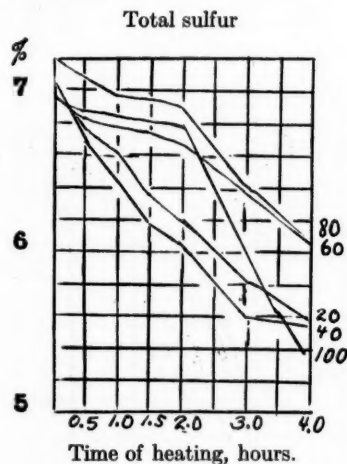


Figure 3

Numbers indicated on the curves are the times of vulcanization (in minutes) of samples.

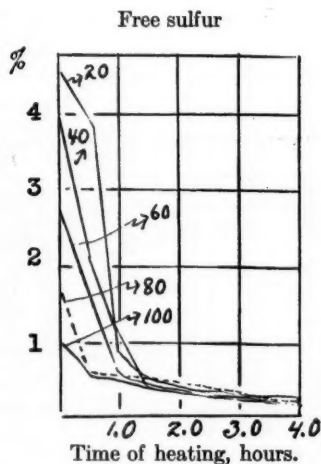


Figure 4

TABLE IV

Sample	Percentage	Duration of Heating (Hours)							
		0	0.5	1.0	1.5	2.0	3.0	4.0	
A	Total S	7.02	6.74	6.60	6.33	6.17	5.79	5.56	
B	Total S	7.04	6.65	6.43	6.15	6.03	5.75	5.45	
C	Total S	6.95	6.80	6.72	6.72	6.65	6.35	6.03	
D	Total S	7.19	...	6.94	...	6.88	6.38	6.09	
E	Total S	6.88	...	6.83	...	6.76	5.94	5.30	
A	Free S	4.56	3.97	0.80	0.48	0.36	0.27	0.22	
B	Free S	3.90	2.13	0.99	0.39	0.28	0.19	0.14	
C	Free S	2.60	1.60	0.52	0.42	0.32	0.20	0.12	
D	Free S	1.68	0.56	0.52	...	0.42	...	0.14	
E	Free S	1.00	0.52	0.46	...	0.26	...	0.12	
A	Combined S	2.46	2.77	5.80	5.85	5.66	5.52	5.34	
B	Combined S	3.14	4.52	5.44	5.76	5.75	5.56	5.31	
C	Combined S	4.35	5.20	6.23	6.30	6.33	6.15	5.94	
D	Combined S	5.51	...	6.42	...	6.46	...	5.95	
E	Combined S	5.88	...	6.37	...	6.50	...	5.18	
A	Resinous substance	3.79	13.62	25.03	22.89	15.69	11.45	9.93	
B	Resinous substance	4.67	22.76	19.23	19.83	13.29	9.97	7.57	
C	Resinous substance	3.63	15.76	21.59	15.31	12.76	8.38	6.63	
D	Resinous substance	2.80	22.00	19.40	...	12.90	...	6.90	
E	Resinous substance	3.93	18.58	18.88	...	14.02	...	6.93	

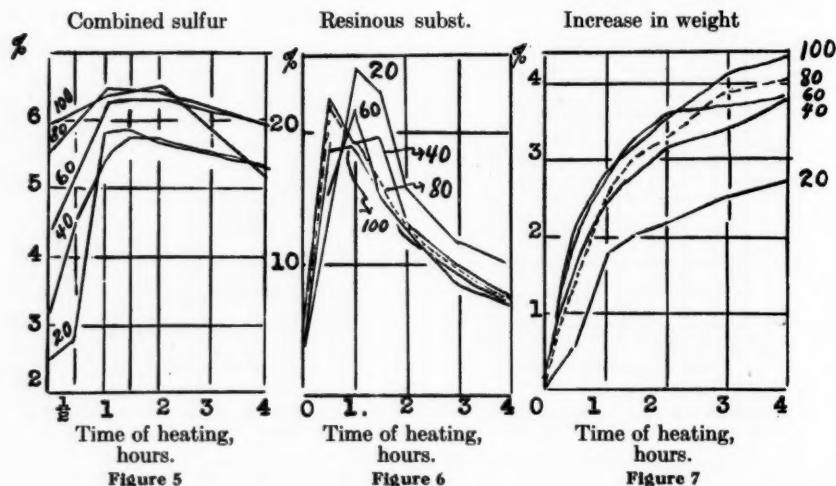
A, B, C, D, and E are the samples vulcanized for 20, 40, 60, 80, and 100 minutes, respectively.

TABLE V

Sample	Percentage	Duration of Heating (Hours)					
		0.5	1.0	1.5	2.0	3.0	4.0
A	Increase in weight	0.58	1.74	2.02	2.16	2.50	2.72
B	Increase in weight	1.52	2.36	2.80	3.14	3.36	3.74
C	Increase in weight	2.00	2.73	3.24	3.58	3.64	3.76
D	Increase in weight	1.26	2.42	3.00	3.22	3.84	4.04
E	Increase in weight	1.92	2.75	3.18	3.51	4.08	4.32

TABLE VI

Duration of Heating (Hrs.)	Percentage Acetone Ext.	Percentage CHCl <sub>3</sub> Ext.	Duration of Heating (Hrs.)	Percentage Acetone Ext.	Percentage CHCl <sub>3</sub> Ext.
0	2.49	94.86	2.0	1.75	98.35
0.5	2.00	97.60	3.0	1.57	98.40
1.0	1.90	98.10	4.0	1.37	98.70
1.5	1.80	98.20			



### Discussion of Results

Although the results of each experiment have been presented individually, their interrelation requires discussion under general topics.

#### Acetone Extract

The vulcanized samples not reheated (control) show a gradual decrease in acetone extract with increase in the time of vulcanization up to the optimum, and an increase in the over-vulcanized sample. Though Minatoya and Aoe (*J. Rubber Soc. Japan*, 2, 235-8(1930)) conclude that the acetone extract decreases with the time of vulcanization, our results on over-vulcanized and reheated samples indicate that the acetone extract is a minimum at the optimum time of vulcanization. Our experiments indicate that the acetone extract reaches a maximum at 0.5-1 hour's heating, regardless of differences in the original time of vulcanization. In principle, this is in agreement with Yamazaki and Okuyama (*J. Soc. Chem. Ind. Japan*, 32, 1148(1929)), who found that in aging tests the acetone extract reached a maximum after several hundred hours' heating at 70° C. This is probably due to changes in the solubility in acetone of resinous substance, or perhaps to thermal

decomposition of a part of the rubber to an acetone-soluble form, especially noticeable with over-vulcanized samples.

That the acetone extract decreased rapidly after it reached a maximum value is an important fact which should not be overlooked. This is considered a result of a decrease in the free sulfur by sublimation, a change of an acetone-soluble substance into an insoluble form by union with sulfur or oxygen, and the loss of an acetone-soluble substance by volatilization.

The decrease in acetone-soluble substance of heated raw rubber with increase in the time of heating, as shown in Table VI, may also be attributed to the change of the acetone-soluble substance into an insoluble form by oxidation and partial volatilization. The difference in the acetone extracts between the raw and vulcanized rubber is that the former gave no maximum value while the latter always did; this peculiarity of vulcanized rubber shows at once that the presence of sulfur caused a temporary increase of the acetone extract.

The explanation of this phenomenon, as pointed out by some investigators, may be attributed to the special accelerating action of sulfur on the depolymerization of rubber molecules, or to the formation of a special substance which accelerates the chemical change of rubber molecules or resinous substances by the action of sulfur in vulcanized rubber. It is of interest to give some explanation why free sulfuric acid is produced by the aging of vulcanized rubber, as found by Yamazaki (*J. Soc. Rubber Ind. Japan*, 5, 17(1932)). Accordingly, there is sufficient evidence to explain why vulcanized rubber ages faster than raw rubber.

#### Chloroform Extraction

Hada and Nakajima (*J. Rubber Soc. Japan*, 3, 13(1931)) showed that the maximum chloroform extract was not reached even after 16 hours of extraction, but it increased with an increase in the time of extraction. They thought that a 4-hour extraction is satisfactory for practical purposes. In our work, the maximum extract was obtained by a 20-hour extraction. There seems to be a limit to the yield of chloroform-soluble depolymerized rubber by the action of heat during extraction. The results of the chloroform extraction of vulcanized rubber without heat treatment showed that the amount was larger in under- and overvulcanized rubbers and less at the point of optimum vulcanization, as also shown by Minatoya and Aoe. Vulcanized samples with heat treatment gave a maximum amount of extract after about 0.5 hour of heating and this then decreased rapidly with an increase in time; this is consistent with the increased chloroform extract in overvulcanized rubber with no heat treatment. The existence of a maximum extract is due to depolymerization of the rubber or to the formation of chloroform-soluble substances by the decomposition of rubber during the heating. A rapid decrease in the extract after reaching a maximum value is due to the formation of insoluble substances by the revulcanization of depolymerized rubber or by oxidation. There is no contradiction with the results shown in Table VI, in which the chloroform extract of the milled raw rubber increased with an increase in the time of heating.

These facts demonstrate clearly that there is a definite limit to the temperature and to the time of heating which must not be exceeded in the reclamation of rubber.

The appearance of a maximum chloroform extract gives not only a theoretical explanation of the mechanism of reclaiming of rubber, but also gives a clear view of the phenomenon of the aging of rubber. Ordinarily the aging of rubber is attributed to oxidation of the rubber molecules; but the authors have come to the conclusion, from these studies of changes in the solubility of the products in acetone and chloroform by heating, that this so-called "oxidation," the most important



phenomenon in aging, is a change in chemical structure of the rubber molecule produced by heat in the presence of oxygen and sulfur.

#### **Change in Total Sulfur**

Due to the loss by sublimation, the total sulfur content decreased on heating. The rate of loss was greater in undervulcanized samples, as indicated in the tables and figures, and three characteristics are to be noted: the extract of undervulcanized samples decreased rapidly soon after heating, the extract of optimum vulcanized samples decreased gradually, and the extract of overvulcanized samples decreased gradually up to 2 hours of heating, whereas the decrease was very rapid after this time. These phenomena can easily be explained by the tendency of free sulfur to decrease, and by the structural change in the rubber molecules by combination with oxygen and sulfur. The decrease in the total sulfur during the heating of rubber is due to sublimation, and partly to a loss as hydrogen sulfide formed by decomposition during the heating, as already indicated recently by Wollensky.

#### **Change in Free Sulfur**

A considerable decrease in free sulfur was noted. This is also attributed, at least in part, to sublimation and in part to a combination of sulfur with the rubber.

#### **Change in Combined Sulfur**

This was calculated from the differences in the total and free sulfur. The combined sulfur showed also a maximum value at a certain time during the heating, which indicates that vulcanization progresses up to this point. This is in agreement with the fact that the maximum combined sulfur appears after the appearance of the maximum acetone and chloroform extracts. The combined sulfur diminishes after the appearance of a maximum point for the same reason as does the total sulfur.

#### **Change in Resinous Substance**

The resinous substance showed an increase during the heating and reached a maximum value after a certain time. This fact has already been discussed under the subject of acetone extract.

#### **Change in Weight**

The samples increased considerably in weight with an increase in the time of heating. An increase in weight, in spite of the decrease in free and combined sulfur, must be attributed entirely to oxidation. The progress in oxidation is also explainable by the fact that the acetone and chloroform extracts became less than those of the control samples, and that the rubber lost its viscous nature, changing to a brittle mass. The rate of increase in weight of the samples was greater in the case of over-vulcanized samples.

#### **Summary**

By heating samples of a rubber-sulfur system at 160° C., the following results in relation to the time of heating were obtained:

1. The maximum acetone extract was obtained after 0.5-1 hour of heating, and the amount decreased rapidly thereafter with increase in the time of heating until it became equal to or less than that of the control samples.
2. The maximum chloroform extract was obtained after 0.5 hour of heating, beyond which the amount decreased rapidly until it was less than that of the control samples.

3. The amount of total sulfur decreased, and this tendency to decrease is to be attributed to three factors.

4. There was also a rapid decrease in free sulfur.

5. The maximum combined sulfur content was reached after a certain time of heating, beyond which it decreased. The maximum point was reached after the acetone and chloroform extracts had reached their maximum values.

6. The maximum content of resinous substance was also obtained after a certain time.

7. The weights of the samples increased during the heating, and this increase was greater in over-vulcanized samples.

A general discussion of these experimental findings leads to the conclusion that the processes of aging and reclaiming of rubber may both be attributed to a change in the chemical structure of the rubber molecules produced by heat in the presence of sulfur and oxygen.

This investigation is an outcome of our work on reclaimed rubber. Thanks are due to Prof. Y. Tanaka for his kindly advice.

# The Production of Isoprene from Rubber

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For more than a century, researches have been carried out on the distillation of rubber, and the general nature of the products—*isoprene*, *terpenes*, and higher *terpene* compounds—has long been known, but comparatively little work has been done on the effect of variations in the conditions of distillation, and in particular on the maximum possible yield of *isoprene*.

Williams (*Phil. Trans.*, **150**, 241 (1860)), using an iron retort and distilling rubber at a relatively low temperature, obtained some 5% of crude *isoprene*, b. p. 37–44°. Fischer and Harries (*Ber.*, **35**, 2156 (1902)) showed that when rubber is distilled at 0.25 mm., less than 1% of *isoprene* is obtained, and Staudinger and Fritsch (*Helv. Chim. Acta*, **5**, 785 (1922)), working at 0.1–0.3 mm. and 275–320°, obtained 3.1%. These two results are not quite consistent, but they tend to show that a low pressure militates against a high yield of *isoprene*.

Staudinger and Geiger (*Helv. Chim. Acta*, **9**, 549 (1926)) distilled rubber at ordinary pressure in an atmosphere of carbon dioxide and obtained 4.3% of crude *isoprene*. They also showed that rubber changes on heating, rapidly above 270°, to a "polycyclo-rubber," which is more stable than ordinary rubber and does not yield *isoprene* on distillation. Midgley and Henne (*J. Am. Chem. Soc.*, **51**, 1215 (1929)) distilled large quantities of rubber (200 lb.) in 16-lb. batches by quickly raising the temperature of the retort to 700°. They thus obtained a 10% yield of *isoprene*, together with the three isomeric 2-methylbutenes resulting from its reduction, which occurred in the same fraction.

The very extensive work on the production of *isoprene* from *terpenes* has given rather contradictory results. By far the best yields claimed are those obtained by the method of Ostromisslenski (French Pat. 442,980, 21/3/12) from dipentene, turpentine oil, etc. The method consists in boiling a mixture of the *terpene* and some low-boiling solvent, such as benzene, so that the vapor of the *terpene* is produced below its boiling point. The mixed vapors are then passed over hot metallic wires and the products removed continuously. The vapors are produced at 95–115°, and the yield is stated to be 80–90%.

In the present work an attempt was made to obtain the maximum yield of *isoprene* (1) from rubber directly, and (2) from the higher-boiling fractions obtained as by-products in (1). Various methods of distillation were tried, and the best results were obtained by dropping pieces of solid rubber on a hot surface and quickly removing and cooling the products. In this way a yield of 16.7% of pure *isoprene* was obtained. The higher-boiling fractions from this process were treated in various ways to obtain *isoprene*, and the best results came from a modification of Harries's "isoprene lamp." By combining the two processes, a total over-all yield of 23% was obtained.

We encountered much difficulty in estimating *isoprene* by the methods at present in use, none of which was entirely satisfactory. We now describe a new method, based on the Diels-Alder reaction with maleic anhydride, which gives accurate results when applied to mixtures not containing other butadienes. The presence of amylenes does not affect the results, which are definitely better than those

obtained by the methods of Ostromisslenski (*J. Russ. Phys.-Chem. Soc.*, **47**, 1983 (1915)) or Lebedev and Yakubchik (*J. Chem. Soc.*, 1928, 823).

### Experimental

The rubber used was either smoked sheet or crepe, of the following analysis (%):

	Moisture	Ash	Protein	Resin	Rubber
Smoked sheet.....	0.52	0.34	2.18	2.93	94
Crepe.....	0.79	0.14	2.04	2.02	95

All the final percentage yields are calculated on the weight of raw rubber used. The type of retort employed is indicated under each experiment. Condensation was effected by ice-salt, and frequently it was necessary to use two condensers in series. Temperatures were ascertained by a thermocouple, and were generally determined at the conclusion of an experiment.

*"Standard Distillation."*—For purposes of comparison, 250 g. of rubber were distilled from an iron retort of 2-l. capacity during 4 hours, the temperature being gradually raised to 580°. In this, and in all other distillations, the distillate was divided into four fractions: (1) up to 60°, containing isoprene; (2) 60–110°, containing  $C_6H_6$ , etc.; (3) 110–200°, containing dipentene and other terpenes; and (4) the remainder, containing polyterpenes, etc. The comparative amount of (2) indicated to some extent whether extreme pyrolysis with its consequent secondary changes had occurred, since when the distillate was produced at higher temperatures, this fraction increased.

Mean values for the "standard distillation" were: Total distillate, 94.5%. Fractions (1) 9.5%, (2) 5%, (3) 30%, (4) 50%. Fraction (1) contained 82.5% of isoprene.

*Rapid Distillation.*—The same procedure as before was followed, except that the temperature was raised as rapidly as possible to 650°. The whole operation occupied about 25 minutes. The mean result was: Total distillate, 94.5%. Fractions (1) 14.6% (83.6% of isoprene), (2) 3.1%, (3) 27.8%, (4) 49%. This result confirms the work of Midgley and Henne (*loc. cit.*).

*Determination of the Point at Which Isoprene Is Evolved.*—The two experiments were repeated, but the distillate was collected in several cuts; with a slow distillation the whole of the isoprene came over in the first half of the time and the first 70% of the distillate. With a rapid distillation, however, isoprene occurred in all but the last of the cuts and in 90% of the total distillate.

*Distillation of Rubber Solutions.*—Solutions of rubber in fraction (3) were dropped slowly into a heated copper retort. The best results were obtained from a 10% solution but only represented a 5.5% yield of fraction (1), the isoprene arising from the solvent being allowed for by means of a blank experiment.

*Distillation of Molten Rubber.*—Rubber was heated slowly till decomposition had proceeded far enough to permit of the residue being sufficiently fluid to flow at about 150°. Some distillate was collected during this heating, and the fluid residue maintained at about 150° was dropped slowly into a heated copper retort. The best results were obtained at about 600°, and under these conditions the total yield of fraction (1) was 11.6%. The process is slow and clearly has no advantage over a direct distillation.

*Distillation of Solid Rubber.*—For this distillation an apparatus was devised consisting of two pieces of iron tube joined at right angles. The limbs were about 18 inches long and the internal diameter 1 inch. Sheet-iron condensers were fitted on both limbs, and the apparatus was clamped so that one limb was horizontal and the other vertical. Fixed into the top of the vertical limb was a long

glass tube (the inside tube of a condenser) closed at the upper end by a cork. The horizontal limb was connected to the condensing system.

To operate the retort, the joint between the two limbs, *i. e.*, the bottom of the vertical limb, was heated to the required temperatures, and small pieces of rubber were dropped down the glass tube by removing and quickly replacing the cork. By this means the solid rubber, without any preliminary heating, was brought practically instantaneously to the temperature of the retort. The volatile products were removed quickly, and any tendency for the vapors to escape through the glass tube prevented by applying slight suction (about 3 mm. below atmospheric pressure) to the end of the condensing system. The sheet-iron condenser on the horizontal limb of the retort cooled the vapors quickly below the temperature of about 300°, at which isoprene polymerizes to dipentene with any appreciable velocity.

In these experiments, 100 g. of rubber (cut to 1-g. pieces) were used, and a distillation occupied about 1½ hours. Experiments were carried out over a wide range of temperature and the optimum temperature was found to be 590–600°, the yields falling off rapidly on both sides. Typical results were as follows:

	Total Distillate, %	Fractions, %			
		(1)	(2)	(3)	(4)
540°	89	16.5	5.6	29.4	37.5
570	88.1	18.5	6.2	30.3	33.1
600	86.8	19.9	6.5	27.9	32.5
610	86.1	18.3	6.9	27.6	33.3
650	76.1	15.1	8.0	23.9	29.1

Fraction (1) contained an average of 84% of isoprene and this gives a maximum yield of 16.7% of isoprene from the distillation of the rubber. The highest yield previously recorded was 10%, and as the isoprene was separated only by fractionation (Midgley and Henne, *loc. cit.*), it was probably not quite pure.

*Cracking of Fractions (3) and (4).*—Attempts were then made to obtain isoprene from fractions (3) and (4) by, in general, the methods usually employed in similar work on the terpenes. The figures recorded below refer in each case to the optimum temperature.

(a) Fractions (3) and (4) separately dropped slowly into the iron tube retort at 580–610° gave 7.2 and 4.4%, respectively, of fraction (1), which now contained only 72% of isoprene.

(b) An emulsion consisting of 100 g. of fraction (3) with 50 g. of H<sub>2</sub>O dropped slowly into a heated copper retort, gave 6.8% of fraction (1) at 600–650°, and fraction (4) under similar conditions gave 3.6% of fraction (1) at 630–650°. It had been hoped that the steam produced would help to remove the vapors more quickly from the hot zone, but there was no advantage in the method.

(c) The vapor of fractions (3) and (4), passed separately through a heated silica tube, gave 7.5 and 4.4% respectively, of fraction (1) at 580–610°.

(d) The vapor of fractions (3) and (4) was passed over a heated platinum wire in an apparatus similar to the "isoprene lamp" of Harries and Gottlob (*Ann.*, 383, 228 (1911)). A coil was made consisting of 1 m. of 0.01-inch platinum wire wound on mica formers. This was suspended in a 1-l. Pyrex flask in such a position that the returning reflux liquid did not fall on the wire. The best results were obtained by using a current of 4.0–4.2 amps. at 200 volts, the distillate being taken from the top of an air-cooled reflux condenser. One hundred grams of fraction (3) required 1 hour's treatment, and the yield was 17.4% of fraction (1), containing 78.2% of isoprene. The higher-boiling portions of the distillate were



retreated 3 or 4 times, giving decreasing yields each time, the total yield being 21.8% of fraction (1) and 17.2% of pure isoprene. Fraction (4) treated in the same way yielded very little isoprene. A very slight improvement in yield was obtained by diluting fraction (3) with  $C_6H_6$  (cf. Ostromisslenski, *loc. cit.*).

Combining the yields from the above process with those from the distillation of solid rubber, a total yield of 23% of pure isoprene was obtained, calculated on the rubber used.

*The Estimation of Isoprene.*—Exhaustive experiments on the dichloro-compound method of Ostromisslenski and the sulphone method of Lebedev and Yakubchik showed that they give low results. By fractionation it is difficult to get strictly pure isoprene, and, moreover, during the process there is some loss by polymerization. We therefore attempted to apply the Diels-Alder reaction for purpose of estimation. The procedure adopted is essentially that of Farmer and Warren (*J. Chem. Soc.*, 1931, 3221). A weighed quantity of the mixture to be estimated was distilled from sodium to remove traces of water. About 10 g. of pure  $C_6H_6$  were weighed into a tared, well-stoppered bottle, about 2 g. of the mixture added, the whole weighed, and immediately placed in ice-salt. Just over 4 g. of commercial maleic anhydride (m. p.  $54^\circ$ ) (rather more than twice the expected weight of isoprene in the mixture) were weighed into a beaker and warmed with about 10 g. of pure benzene until dissolved. The solution was cooled and poured into the tared bottle, which was immediately stoppered and returned to the ice-chest for 12 hrs. The exact weight of maleic anhydride added was found by evaporating the few drops of  $C_6H_6$  left in the beaker, weighing the residue, and subtracting this from the original weight taken. The contents of the bottle were next transferred to a Carius tube, and the sealed tube heated at  $100^\circ$  for 2 hours. After cooling, the contents of the tube, together with the  $C_6H_6$  washings, were evaporated at room temperature and reduced pressure. On adding pure dry ether to the residue and again evaporating in the same way, dry white crystals were obtained and weighed. The gain in weight of the maleic anhydride represented the weight of isoprene present in the original mixture.

The method was tested by preparing strictly pure isoprene from the sulphone and then estimating its purity. Duplicate experiments in each case gave a result of exactly 100%. Further, mixtures were made of this pure isoprene with amylenes, and the results confirmed the accuracy of the method. Details of one determination are given:

Mixture	Amylenes	1.5120 g.	Maleic anhydride	4.2613 g.
	Isoprene	1.7925 g.	Compound recovered	6.0534 g.
			Isoprene found	1.7921 g.

## Some Aspects of Plasticity and Its Determination

G. W. Usherwood

### Introductory

In recent years the importance of plasticity in determining the ease with which a rubber stock can be processed has become increasingly realized, and several methods for its measurement have been devised. Before examining any of the methods employed for its measurement, it is advisable to consider what is meant by plasticity, since much loose and contradictory usage of the term exists in the rubber industry. The common meaning of plasticity refers to those characteristics of matter which have to do with the receiving and holding of form. A body is said to be plastic or possess plasticity when it can be permanently deformed by any force exceeding a definite minimum.

The difference between a viscous substance such as pitch and a plastic substance such as clay is that the former slowly changes its shape under the smallest applied load, that is, its own weight, while the latter requires some force above a minimum before it will deform.

In practice one must distinguish between two substances which, although soft and yielding with equal ease to any deforming force, differ widely with the fidelity with which they retain the deformation imparted. One may retain its deformed shape accurately and permanently, as, for example, a piece of sculptor's clay, while the other may, after some interval of time which may be long or short, resume to a considerable extent its original form, as, for example, a piece of masticated rubber. In the first case the clay is said to be more plastic than elastic, while in the second the rubber is said to be both plastic and elastic.

It is, therefore, somewhat surprising to find that the technical use of the term plasticity with a well defined meaning for quantitative considerations has been accompanied by so much confusion. This is no doubt due to its close relationship to other properties of matter wherein it is an important factor, namely, elastic and hardness phenomena on the one hand, and permanent set and viscous flow on the other. Some writers seem to indicate that plasticity is synonymous with softness (Maxwell, "Theory of Heat," p. 295, 1883) or permanent set (Van Rossem and Van der Meyden, *Rept. of International Congress on Testing Materials*, 1927), while others consider the flow involved is of paramount importance, and confusion with viscosity has resulted (Bingham, "Fluidity and Plasticity," p. 4, 1922; Dietrich, *Ind. Eng. Chem.*, 21, 768 (1929)). Van Rossem and Van der Meyden (*loc. cit.*) have pointed out that plasticity involves more than deformation—the amount of recovery is an essential element. Karrer (*Ind. Eng. Chem.*, 21, 770 (1929)), therefore, defines plasticity as "the susceptibility to and the retention of deformation." In this definition both softness and permanent set are considered.

There are two general methods by which the plasticity of rubber has been measured, namely, extrusion methods and compression methods. In the extrusion method the rate at which rubber is extruded from a small orifice under some definite load is measured. With this method viscosity is considered to be the most important factor in determining plasticity. The plasticity of masticated rubber when measured by this method as Martin (*Trans. Inst. Rubber Ind.*, 6, 298 (1930)) has

shown does not conform to the ideal curve for a plastic substance as determined by Bingham (*loc. cit.*). This is no doubt due to the fact that no account is taken of the elasticity of the masticated rubber, and that Bingham's ideal curve was worked out for paints, where the recovery is practically nil.

With the compression methods for measuring plasticity that due to Williams (*Ind. Eng. Chem.*, 16, 232 (1924)) appears to be the most widely used. In the original Williams method a sphere of rubber was compressed under a fixed load, and the thickness was measured after some suitable interval of time. In this method the softness or compressibility of the rubber is taken as being the most important factor in determining plasticity. But as has been previously stated, plasticity is not a simple function of softness alone, permanent set is a factor which must be considered. To this end the Williams' method has been modified by Grenquist (*Ind. Eng. Chem.*, 22, 759 (1930)) and others, so that the recovery under no load could be measured.

Karrer (*loc. cit.*), considering plasticity as an integral property of a material, suggested a quantitative definition of plasticity which reads: "A substance has unit plasticity which deforms a definite amount under some standard conditions when a force of 1 kg. per sq. cm. acts upon it for one second and the whole of the deformation is retained," and devised an instrument for measuring plasticity which conformed to this definition. It is obvious that unless a complicated power driven plastometer similar to that designed by Karrer (*Ind. Eng. Chem., Anal. Ed.*, 1, 158 (1929)) where the deforming force or weight is actuated by a motor and spring it is impossible to arrange for the deforming force to act only for one second and so fulfil the conditions of the above definition. If, however, the definition is modified so that the deforming force is allowed to act for a longer but definite period of time a much simpler instrument for measuring plasticity can be designed.

A plastometer embodying the above principles has been designed. It is somewhat similar to the modified Goodrich plastometer (Karrer, Davies, and Dietrich, *Ind. Eng. Chem., Anal. Ed.*, 2, 96 (1930)).

#### Description of Instrument

The instrument (Fig. 1) consists essentially of the following parts: the lower loading platen (2) on which the cylindrical rubber test pieces are placed. The upper loading platen (3) attached to the gage connecting rod (4) and sliding between bearings (23) in the compression tube (22) which carries the weight (19) which can be raised or lowered by the lever (21) and held in the "up" position by the catch (27). The gage connecting rod (4) and upper loading platen (3) are balanced by the lever and weight (18). The upper end of the gage connecting rod (3) rests on the foot of the gage (5), which can be adjusted for zero error by the clamping screw (26). The upper and lower platens are circular and 1 sq. cm. in area; the weight (19) and compression tube (22) are so adjusted that the load on the test piece is 1 kg., which can be increased to 2 kg. if desired by the addition of lead shot to the weight which has been made hollow. The gage used is a standard micrometer gage reading in 0.01 mm., and having a travel of 10.6 mm.

A heating chamber surrounds the test-pieces and maintains them at any desired temperature. The outer shell (9) of the heating chamber (10) is cylindrical, 6 inches in diameter and 7 inches high. To stop radiation losses this is lined with asbestos (8) and tinned sheet iron (7). The shell is equipped with a glass window (15) 2½ inches wide and 2 inches high, and a funnel-shaped aperture permits of the insertion of test-pieces. The heating chamber proper is cylindrical, 2 inches in diameter and 2 inches high, made of sheet iron with a transit board top and bottom.

The resistance coil (12) is of nichrome wire laced between insulators (11) on the top and bottom transit boards and connected to terminals (13) in the bakelite base (1) for connection to a 110 volt direct current supply. To maintain the heating chamber at 100° C. an adjustable external resistance of 49 ohms is placed in series with the supply.

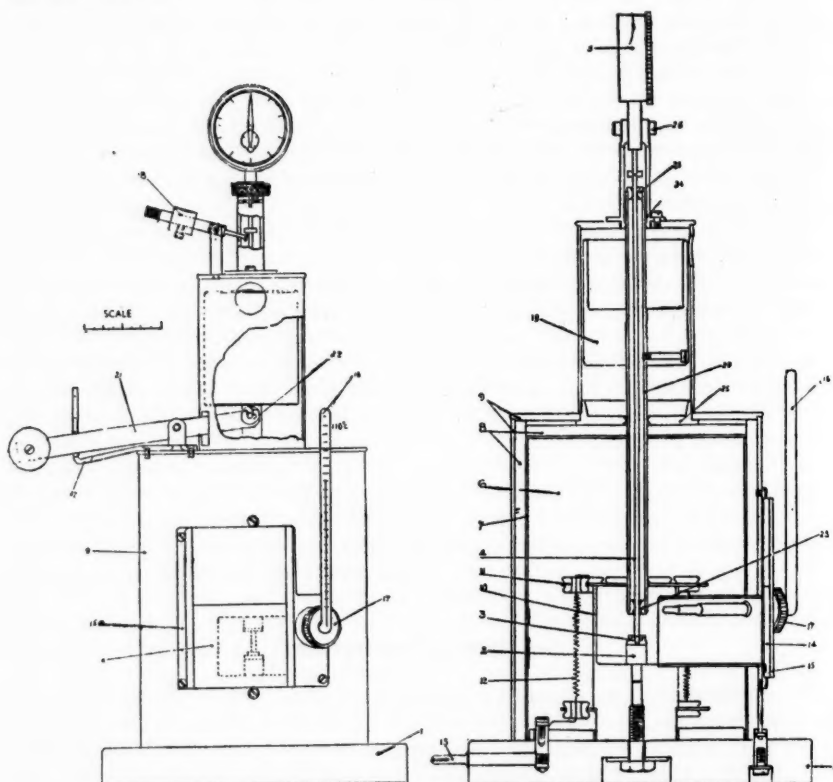


Figure 1

- |    |                          |    |  |
|----|--------------------------|----|--|
| 1  | Circular base.           | 15 | Window frame.                          |
| 2  | Lower platen.            | 16 | Thermometer.                           |
| 3  | Upper platen.            | 17 | Thermometer packing gland.             |
| 4  | Gage connecting rod.     | 18 | Gage rod balance weight.               |
| 5  | Gage, indicates 0.01 mm. | 19 | Compression weight, 1 kg.              |
| 6  | Furnace.                 | 20 | Compression tube.                      |
| 7  | Inner shell.             | 21 | Lever for raising weight.              |
| 8  | Lining, asbestos.        | 22 | Roller.                                |
| 9  | Outer shell.             | 23 | Gage rod bearings.                     |
| 10 | Heating chamber.         | 24 | Upper bearing.                         |
| 11 | Insulators.              | 25 | Lower bearing.                         |
| 12 | Heating element.         | 26 | Knurled clamping nut, on tapered screw |
| 13 | Contact pins.            | 27 | Bracket for 21.                        |
| 14 | Window.                  |    |  |

Temperatures are read by the thermometer (16) and can be maintained constant within 2° C. by suitably adjusting the external resistance even allowing for the window to be opened every 2 minutes for insertion and removal of test-pieces when conducting tests.

### Method of Cutting Test-Pieces

The test-piece used is a right circular cylinder 1 sq. cm. in cross-sectional area and 1 cm. high. To cut this test-piece, a special cutter and trimmer have been designed for fitting to a high speed electric drill, which is mounted horizontally on the bench. The cutting tool is a cylindrical cutter 1.13 cm. in diameter with a widened portion for removing the cut pieces and a  $\frac{5}{16}$  inch shank for fitting into the drill. The sample of rubber from which the test-piece is to be cut is held against the sharp edge of the cutter, backed by a piece of soft vulcanized rubber and well lubricated with water, care being taken that undue pressure is not exerted, otherwise the sample will be scorched.

The holder (Fig. 2) for trimming consists of a tube (1) with a portion of its length (2) removable for the insertion and removal of a test-piece and held in position by a brass ring (3). The tube is fitted with an inner rod (4) moved by the catch (5), and acts as a length stop. The test-piece with one end protruding is inserted in the trimmer with the stop (4) in the back position, the drill started and the end

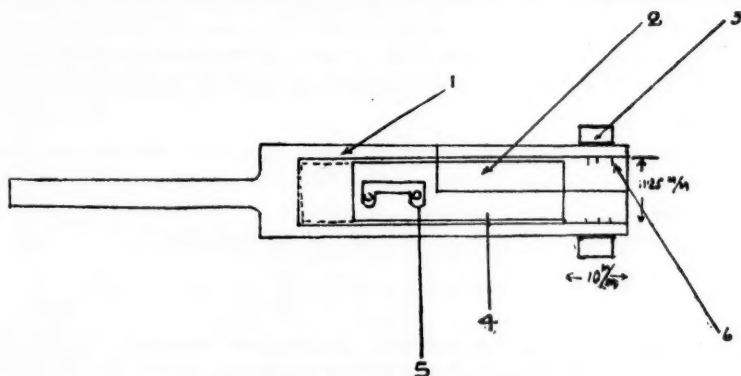


Figure 2—Trimmer for Test-Pieces

- |  |   |
|--|---|
| 1 Outer tube.                            | 4 Inner rod—shown in forward position.    |
| 2 Half portion of outer tube, removable. | 5 Slot and pin for moving the inner rod.  |
| 3 Brass ring holding (2) in position.    | 6 Pins to prevent rotation of test-piece. |

cut off straight with a razor well lubricated with water. The test-piece is then removed and stop (4) moved up to the forward position so that the distance from the end of the trimmer to the stop is exactly 1 cm.; the test-piece is inserted with its trimmed end up against the stop and its other end cut off in a similar manner to that already described. Rotation of the test-pieces is prevented by the small pins (6)  $\frac{1}{16}$  inch long.

### Method of Conducting Tests

The heating chamber of the plastometer is brought to the temperature at which the tests are to be conducted, usually  $100^{\circ}\text{C}$ . The test-pieces are preheated for 15 minutes in an oven at the same temperature and then transferred four at a time to the heating chamber of the plastometer, and allowed to remain for 5 minutes to attain the temperature of the chamber. Small circles of thin rice paper are used to cover the top and bottom of the test-pieces to prevent them sticking to the platens. The test-piece is accurately centered between the platens and its initial height read from the gage after 5 seconds; the weight is then released and height of the test-piece read after 30 seconds' compression. The weight is then removed



and the height of the test-piece read after 30 seconds' recovery, the time being taken with a stop-watch.

Compression and recovery periods have been standardized at 30 seconds, since it is impossible to obtain accurate readings of the compression height in a shorter interval of time because of the speed of the movement of the gage.

Plasticity has been defined as softness times retentivity. The softness expressed in terms of the change of height is:

$$S = f(t.F) \frac{h_0 - h_1}{\frac{h_0 + h_1}{2}} = K \frac{h_0 - h_1}{h_0 + h_1}$$

Where  $F$  is the applied load (1 kg.),  $h_0$  the initial height after 5 seconds' compression by the gage foot, and  $h_1$  the height after 30 seconds' compression by the weight (1 kg.),  $h_0 - h_1$  is the total amount of deformation in time  $t$  (30 seconds), and as a

first approximation  $\frac{h_0 + h_1}{2}$  is the average height of the test during deformation.

Retentivity is defined as the ratio of the amount of deformation retained to the amount of deformation given, and as expressed in terms of height of the test-piece is:

$$R = \frac{h_0 - h_2}{h_0 - h_1}$$

where  $h_2$  is the height after 30 seconds' recovery.

Plasticity then expressed in terms of height of the test-piece is:

$$P = SR = K \frac{h_0 - h_2}{h_0 + h_1}$$

These formulas give values for plasticity, softness, and retentivity ranging from 0 to 1. The more plastic or soft the rubber stock, the nearer the plasticity or softness approaches unity.

The exact mathematical interpretation of the expression  $(t.F)$  for softness has not yet been worked out, and several other formulas for expressing softness in terms of height of the test-piece have been suggested, such as:

$$\log_{10} \frac{h_0}{h_1}; \quad \frac{h_0 - h_1}{h_0}; \quad \frac{h_0 - h_1}{h_1}.$$

All give values of the same order as the expression in the above formula.

The advantages of the new instrument may be summarized as follows. The gage is not heated when tests are being conducted, consequently inaccuracies due to a sticking gage are overcome. Temperature can be accurately controlled. The whole of the weight except that due to the gage spring can be practically instantaneously removed so that the recovery can be readily measured. The test-pieces are of a definite initial height and volume, since earlier work with a Williams' plastometer had indicated that to obtain concordant results the initial height of the test-pieces was as an important a factor as the volume. The pressure applied by the load is constant during the whole of the time of its application, and does not gradually decrease as in the Williams' method. Van Rossem has shown that more consistent results could be obtained by modifying the Williams' method so that the weight acted only on a definite area. Having the platens of the instrument the same area as the test-piece has the added advantage that they are always more

nearly parallel to one another, and test-pieces can be more accurately centered between them.

### Typical Results

Under this heading are given a few results of tests conducted on tread stocks and the carbon black master batch used for the tread stocks, which show how the plasticities of the raw stocks can affect the physical properties of the vulcanized products.

In Table I are given the relative plasticities, softnesses, and retentivities of a 66 per cent carbon black master batch stock milled on a 60-inch mill for various times, with different settings of the rolls. The plasticities were taken on the plied-up stocks 24 hours after mixing and were measured at 100° C., the samples being preheated for 20 minutes. The letters A, B, C, D refer to the set of the rolls during milling.

Stock A—the rolls were set at  $\frac{3}{16}$  inch during the whole of the time of milling.

Stock B—the rolls were set at  $\frac{1}{4}$  inch during the breaking-down of the rubber and the addition of black and  $\frac{3}{16}$  inch during mixing and batching-off.

Stock C—the rolls were set at  $\frac{3}{8}$  inch during the breaking-down of the rubber and the addition of black and  $\frac{3}{16}$  inch during mixing and batching-off.

Stock D—the rolls were set at  $\frac{3}{16}$  inch while the rubber was being broken down, opened to  $\frac{3}{8}$  inch during the addition of black, and closed to  $\frac{3}{16}$  inch during mixing and batching-off.

As is to be expected, the results of all four stocks show that the plasticity of the stock increases the longer the time the stock is milled.

TABLE I  
CARBON BLACK MASTER BATCH

Milled on a 60-Inch Mill.		Plasticities Measured at 100° C.		
Stock No.	Time of Milling, Min.	Relative Softness	Relative Retentivity	Relative Plasticity
A	45	22	77	17
	43	21	75	16
	42	20	72	14
	50	19	82	15
B	45	17	80	14
	44	18	79	14
	55	15	73	11
C	42	14	69	10
	40	13	69	9
	36	16	74	12
D	35	14	71	10
	34	13	71	9

It is difficult to incorporate high percentages of carbon black into rubber, due to it flaking and passing through the nip of the rolls without being forced into the rubber. This means that the time required to incorporate the carbon black is often excessive, and over-milling or over-mastication of the stock results. To decrease the time required for incorporating the carbon black and so prevent over-milling, the nip of the rolls was increased during the addition of the carbon black. It was found, however, that little decrease in the time required for the addition of black resulted, though the plasticities as shown by the values given for stocks B and C are lower than for stock A, which are excessively high. In other words, the incorporation of the carbon black into the stocks B and C had been accomplished without the rubber becoming so over-masticated or over-milled as is the case with stock A. This was all to the good, but the time required for milling the batch was still too

long. To reduce further the time of milling, the rubber was broken down with the rolls set at a  $\frac{3}{16}$ -inch nip until it only just formed a smooth blanket round the rolls. The nip was then increased to  $\frac{3}{8}$  inch and the black added; during mixing and batching off the rollers were tightened to a  $\frac{3}{16}$ -inch nip. By this method the black was readily incorporated into the rubber. The plasticities of stock D show that the stock is not as plastic as stock A, B, and C, and that it has not been over-milled in order to incorporate the black. These results go to prove the contention that the best method of incorporating the carbon black into a stock is to grind it in, this grinding being accomplished by not thoroughly breaking down the rubber before adding the black. The reverse is, of course, true of other pigments, they being more readily incorporated if the rubber is thoroughly broken down.

In Table II are given the relative plasticities, softnesses, and retentivities of the tread batches, and extruded treads made up from the batches of black master batch stock just discussed and the lots numbered accordingly. The mean plasticities of the black master batch stocks are also given. Under the same

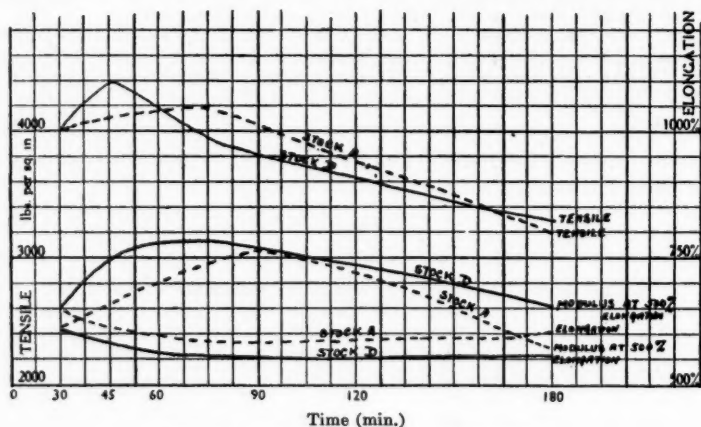


Figure 3—Tread Stocks Cured at 287° F.

conditions all tread batches were mixed on a 60-inch mill for the same time, and the extruded treads were all the same size. The plasticities were taken 24 hours after milling or extruding and were measured at 100° C., the samples being preheated for 20 minutes. The results show how the plasticities of the black master batch stock affect the plasticities of the tread stock and the extruded

TABLE II

Stock No.	Carbon Black Stock			Tread Stock			Extruded Tread		
	Softness	Re-tentivity	Plas-ticity	Softness	Re-tentivity	Plas-ticity	Softness	Re-tentivity	Plas-ticity
A	21	75	16	51	90	46	51	88	45
B	17	80	14	47	88	41	46	85	39
C	15	73	11	46	83	38	48	85	41
D	14	71	10	45	82	37	46	83	39

tread. The lower the plasticity of the the black master batch stock, the lower that of the tread batch and the resulting extruded tread. In Fig. 3 are the tensile curves of the treads. The curve labeled A is that for the tread mixed up from lot A of the black master batch stock, and curve D that for the tread mixed up from lot D of the black master batch. It will be noticed that, although both curves

yield high values for the tensile strength, the optimum cure is different, tread D having its optimum cure at 45 minutes, while the optimum cure for tread A occurs at 60 minutes. Why the difference in optimum cure? Referring back to Table II, it is found that the plasticity of tread D is 39 against the plasticity of tread A of 45. Tread A is soft, its plasticity is high, but it has milled for the same time as tread D. The black master batch stock A has a plasticity of 16, against the plasticity of the black master batch stock D of 10, but as has previously been shown the black master batch stock A was milled for 45 minutes against only 35 minutes for black master batch stock D. Black master batch stock A had definitely been over-worked on the mill, the rubber over-masticated in order to incorporate and thoroughly disperse the black; its "nerve" had gone; it was soft and "flabby," and its plasticity consequently far too high. This, therefore, accounts for the slower rate of cure of tread A compared with tread D, where no over-working of the black master batch stock or tread batch had occurred. Over-milling or over-mastication causes a slowing up of the rate of cure.

These results show how plasticity is a property of a raw stock which cannot be neglected if a uniform product is to be obtained, and how important it is to have an accurate method by which it can be measured.

It is useless, however, to measure plasticities if an accurate and constant control is not kept on milling, calendering, and extruding processes.

In conclusion the author wishes to express his indebtedness to The India Tyre & Rubber Co. (G. B.), Ltd., for permission to publish this paper.

## Plasticity Measurements in the Rubber Industry

J. Behre

TRIER (TRÈVES)

With the growing realization of its importance in factory operations, the plasticity of raw rubber and rubber stocks is being studied more and more. As far as can be seen from the literature, four methods for measuring plasticity are known up to the present time. The most commonly used apparatus is probably that developed by Williams,<sup>1</sup> which depends upon measuring the change in the thick-

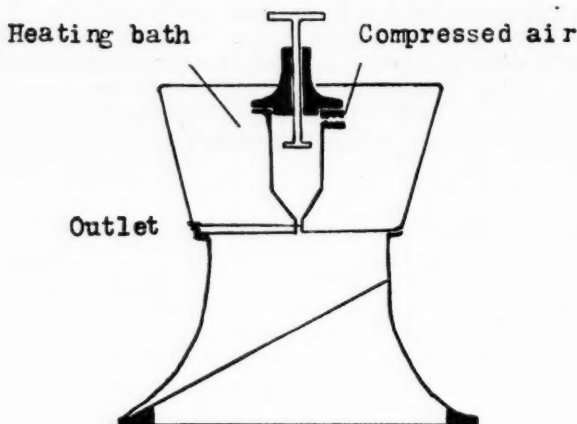


Figure 1

ness of rubber under a load. The same principle is followed in the recently published method of Karrer,<sup>2</sup> except that in this case the elastic recovery is also measured. The other two methods, which were used first by Marzetti<sup>3</sup> and by Griffith,<sup>4</sup> depend on the other hand upon a wholly different principle. Here the rubber or the rubber mixture is extruded through a narrow opening under high pressure and the quantity extruded is measured. Griffith used a dead weight, whereas Marzetti used compressed air to produce the pressure. For several years the author<sup>5</sup> has worked with an apparatus constructed according to the Marzetti principle, and the present paper deals with experiments with this apparatus.

In the first place the apparatus and procedure used in making the measurements should be explained. The apparatus consists essentially of a steel cylinder of about 50-cc. capacity, which becomes smaller at the bottom to which a nozzle 3 mm. in diameter and 20 mm. long is attached. This unit rests in a glycerine bath which is provided with an agitator, and can be heated by electricity. Figure 1 shows schematically the cross section of such a pressure cylinder, while Fig. 2 is a photograph of an apparatus in which 6 pressure cylinders are assembled in one bath. The samples to be studied are placed in the cylinder, which is heated to a definite



temperature, *e. g.*, 80° C., and after the cylinder is closed by means of a spindle, on the lower end of which is attached a disc which is forced against the outlet nozzle to prevent air from flowing past the rubber and escaping out of the nozzle, the charge is forced out with an air pressure of from 10 to 30 atmospheres, according to the hardness of the rubber, and the resulting cord is cut off every 15 minutes and

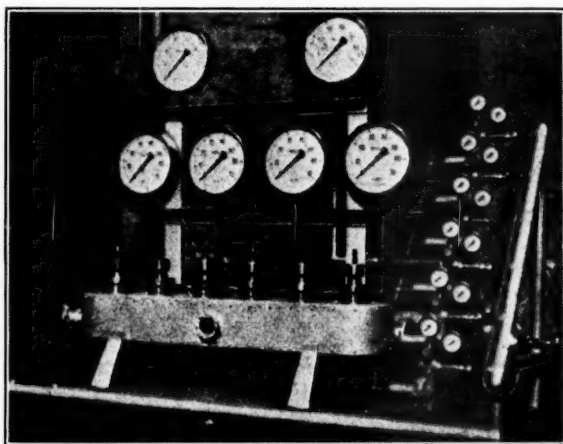


Figure 2

weighed. The first sample is discarded, since experiments show that rubber requires about 10 to 15 minutes to reach the temperature of the medium. Since, according to Marzetti, the quantity extruded is proportional to the square of the pressure, it is appropriate to designate as the plasticity number the square root of the quantity extruded in 15 minutes (in mg.). This number is designated as the  $\sqrt{m_{15}}$ , while that calculated from the volume is  $\sqrt{v_{15}}$ . The pressure and the temperature at which the test was carried out must also be specified.

Now what can be learned by the aid of the plastometer? First of all, the plastometer gives the plasticity of unmasticated raw rubber just as it comes from the plantations, which is of interest to rubber chemists. Greinert and Behre<sup>6</sup> have for their part described in detail variations in the degree of softness, so that at this time it is necessary only to call attention to this publication.

However, in its subsequent progress through the manufacturing operations of milling, mixing, and calendering, the rubber must also be controlled and its plas-

TABLE I  
FIRST LATEX CREPE (10 KG. MASTICATED) COMPRESSED AT 20 ATM. AT 80° C.

Time of Mastication in Min.	Plasticity Number, $\sqrt{m_{15}}$
0 (unmasticated)	0
5	22
10	27
15	34
20	40
25	44
30	44
35	45
	46

ticity measured, so that a uniform product always leaves the milling operations. On the other hand, the test naturally can be used to determine what milling constants, such as the circumferential speed, friction and surface, and what temperatures are best for the mastication of raw rubber and for mixing. This in turn would help in bringing about the highly desirable simplification of types of mills. Tables I to III and Figs. 3 to 5 give the results of a few milling experiments, which

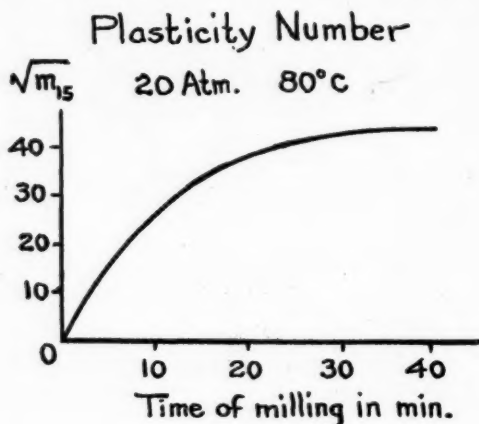


Figure 3

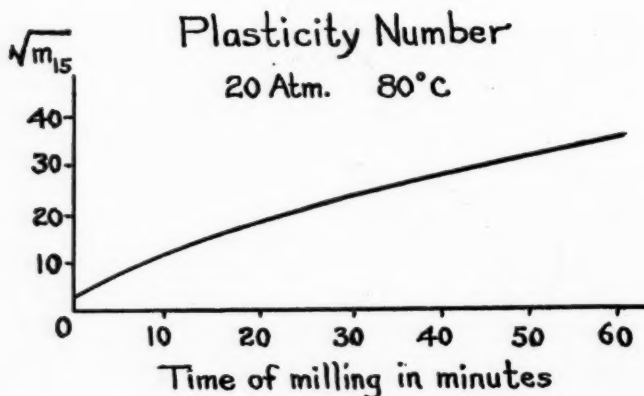


Figure 4

show plainly how much the degree of softness of rubber varies according to the method of milling.

The values in Table I and Fig. 3 show that a hard rubber was used, which when milled in small quantities (10 kg.) softened very rapidly (25 min.). Upon further milling the plasticity increased only very gradually. With 20 kg. of raw rubber on the same mill, in order to reach approximately the same softness as in the first experiment, it was necessary to carry out the mastication in stages, *i. e.*, after 10 minutes the rubber had to be removed from the mill, allowed to cool, and the process repeated for 10 minutes, etc. Even then only after 6 periods of milling for 10

minutes did the rubber reach the same degree of plasticity as in the first experiment after 20 minutes. (See Table II and Fig. 4.)

TABLE II  
FIRST LATEX CREPE (20 KG. MASTICATED) COMPRESSED AT 20 ATM. AT 80° C.

Time of Mastication in Min.	Plasticity Number, $\sqrt{m_{15}}$
0	4
1 time 10	10
2 times 10	16
3 times 10	24
4 times 10	27
5 times 10	34
6 times 10	38

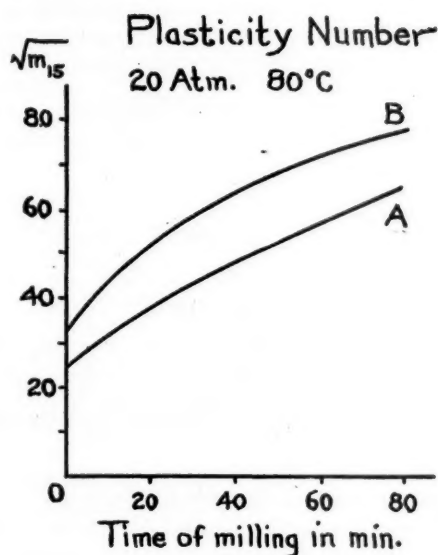


Figure 5

The following table shows the results of another experiment.

TABLE III  
MIXTURE, COMPRESSED AT 20 ATM. AT 80° C.

A		B	
Mixture Prepared from First Latex Crepe		Mixture Prepared from Off-grade Crepe	
Time of Mastication of Raw Rubber in Min.	Plasticity Number of the Mixture, $\sqrt{m_{15}}$	Time of Mastication of Raw Rubber in Min.	Plasticity Number of the Mixture, $\sqrt{m_{15}}$
0	27	0	30
5	29	5	46
10	33	10	46
15	35	15	52
20	42	20	54
25	44	25	58
30	45	30	62
40	47	40	63
60	60	60	74
80	68	80	80

In this experiment which was concerned with friction stocks, first latex crepe, both unmasticated and masticated in stages to 80 minutes, was used in the one case, while in the second case 10 stocks were prepared from off-grade latex crepe which was masticated for the same length of time as the first latex crepe. Here the difference between the two types of rubber, which does not disappear upon prolonged milling, is particularly surprising.

Lastly the results recently published by Bachmann, Behre, and Blankenstein<sup>7</sup> should be mentioned in this connection. Here, for the first time to the author's knowledge, what every practical man has long known has been proved mathematically, namely, that hot mastication causes softening of the rubber much more rapidly than does mastication in cold mills.

TABLE IV  
FIRST LATEX CREPE (1 KG. MASTICATED) COMPRESSED AT 20 ATM. AND 80° C.

Raw Rubber, Masticated at 18° C.		Raw Rubber, Masticated at 65° C.	
Time of Mastication, Kw.-Hr.	Plasticity Number, $\sqrt{m_{15}}$	Time of Mastication, Kw.-Hr.	Plasticity Number, $\sqrt{m_{15}}$
0.6	28	0.6	36
0.8	46	0.8	60
1.0	62	1.0	76

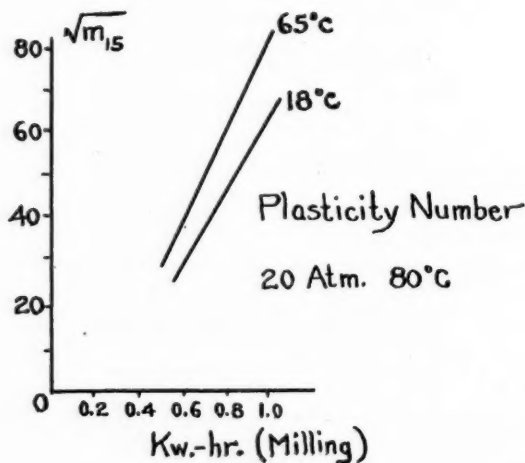


Figure 6

Wholly apart from these measurements, the Marzetti apparatus is an indispensable aid in the laboratory in studying the activity of fillers in rubbers. Table V shows the behavior of different types of black in a mixture, the composition (by weight) of which was as follows:

Rubber	100
Sulfur	4
Diphenylguanidine	1
Zinc oxide	10
Black	40

Here the plasticity number is not the square root of the weight in mg. extruded in 15 minutes, for in this case the plasticity  $\sqrt{v_{15}}$  must be calculated from the

volume, taking into account the specific gravity of the mixture. This is always essential when mixtures of different specific gravities are to be compared with one another.

TABLE V

Sample	Plasticity, $\sqrt{p_{15}}$ 20 Atm. at 80° C.
Carbon Black I	9
Carbon Black II	16
Carbon Black III	19
German Black I	30
German Black II	25
German Black III	29

This table shows the great difference between American gas black and German black, as well as variations within the two groups.

Among inactive fillers, kaolin was chosen because of the fact that several years ago it was believed that some clays conferred to rubber mixtures physical properties which were similar to those obtained with American gas black. The mixtures had the same composition as the mixtures containing black, *i. e.*, 40 parts by weight of kaolin were used with every 100 parts by weight of rubber.

TABLE VI

Sample	Plasticity, $\sqrt{p_{15}}$ 20 Atm. at 80° C.
Kaolin I	40
Kaolin II	48
Kaolin III	36
Kaolin IV	46

Here again great differences are seen in the different kinds of kaolin. If the two tables are now compared, the great differences in plasticity between American gas black and kaolin are immediately evident, and it is seen that even the best grades of kaolin, such as III, have nowhere nearly the toughening action of carbon black.

Like ordinary fillers, softeners play an important role in practical mixing today. It is possible by means of the plastometer to select from the wealth of softeners offered in the trade that which is best suited to the purpose, with the expenditure of little time and money and without waiting for a long series of experiments. Table VII gives a number of such softeners, together with their plasticity numbers. The composition (by weight) of the mixture was:

Rubber	100
Sulfur	4
Diphenylguanidine	1
Zinc oxide	10
Barytes	50
Softener	3

TABLE VII

Sample	Plasticity, $\sqrt{m_{15}}$ 20 Atm. at 80° C
Base mix	80
Base mix + mineral oil	84
Base mix + mineral rubber	86
Base mix + stearic acid	90
Base mix + kautschol	102
Base mix + rosin oil	104
Base mix + oleic acid	106
Base mix + pine tar	112
Base mix + palm oil	146



Finally the accelerator remains to be considered. With the immense number of accelerators of vulcanization available it is very important to study carefully their behavior in compounds. Not only the acceleration of vulcanization, the mechanical properties, color, and aging of the vulcanizate must be determined, but also the critical temperature of the mixture, *i. e.*, the temperature at which a definite type of mixture begins to vulcanize after the addition of any particular accelerator. A knowledge of the critical temperature is of special importance in practice, because there is very often the possibility of premature vulcanization in the case of tubing, hot milling, or calendering. The Marzetti apparatus is of extraordinary value in determining this temperature. In order to determine this temperature, the quantity extruded at 70, 80, 90, 100, and 110° is determined. In this case the extruded material (in cu. mm.) rather than the plasticity number is used directly. The first portion taken off is again discarded, and the quantities extruded after the second and third 15-minute periods are used in the calculation. Table VIII gives the results of the tests of the beginning of vulcanization with three accelerators. The composition by weight of these mixtures was: rubber 100, sulfur 4, accelerator 1, zinc oxide 10.

TABLE VIII

Sample		Plasticity: in Cu. Mm. at 10 Atm.					
		60°	70°	80°	90°	100°	110°
Mixture	Hexamethylenetetramine	...	...	690	1420	...	2220
		...	...	700	1380	...	1610
Mixture	Diphenylguanidine	...	...	450	510	900	..
		...	...	440	480	730	..
Mixture	Vulkazit P	170	230	330	..	...	..
		130	90	0	..	...	..

At 80° C. the second and third portions were practically the same in the accelerator hexamethylenetetramine. At 90° the mass had become definitely more plastic, but still was the same as in the second and third portions. At 110° there was again a distinct rise in plasticity, and at the same time vulcanization had commenced to a slight extent.

With diphenylguanidine as accelerator, vulcanization had already begun at 80° to a slight extent, at 90° it had become distinct, and at 100° it was very distinct.

The accelerator Vulkazit P scorched at a still lower temperature, and even at 60° there was a noticeable diminution of the quantity extruded when the third portion was taken. It may be surprising that the plasticity with the accelerator hexamethylenetetramine was in every case greater than that of diphenylguanidine and Vulkazit P. This is chiefly due to the quality of the raw rubber, which is less plastic with diphenylguanidine and Vulkazit P. It is however due in part to the fact that certain accelerators have a toughening action on the mixture, whereas others have a softening action. This has already been pointed out previously.<sup>8</sup>

Naturally the examination to determine whether vulcanization had begun was always made after the same period of time. As has already been mentioned above, the samples remained in the plastometer for three 15-minute periods. If it is to be established whether a mixture starts to vulcanize after a still longer time, then a fourth and fifth portion must be removed or the mixture must be exposed to a higher temperature for a longer time in the plastometer before the test is made. In most cases a period of 45 minutes will probably be found sufficient for practical needs.

In the foregoing pages the importance of plasticity measurements in the rubber industry has been described. The plastometer is not only a valuable aid for the investigator, but it also serves to extend our knowledge of the behavior of rubber

and its fillers.<sup>9</sup> In the following pages the measurement of the plasticity of rubber will be considered from the scientific standpoint, and at the same time the advantages and disadvantages of the present methods will be compared.

If the plasticity of a substance is to be studied, the concept itself must first of all be clearly understood. When the attempt to define this concept is made, it is found that there is no definite answer. According to general usage, plastic is the same as deformable, and a plastic mass is a body which undergoes a permanent deformation under a definite force.

Recently Karrer<sup>10</sup> has dealt with this problem in detail and in the course of his work he has proposed the following definition: "A substance has unit plasticity that deforms a definite amount under some standard conditions when a force of 1 kg. per sq. cm. acts upon it for 1 second, and the whole of this deformation is permanently retained."

On the basis of this definition of the concept, let us examine whether the methods of measurement now commonly used in the rubber industry are suited to their purpose. The oldest method, that developed by Marzetti,<sup>11</sup> has been described earlier in this article in detail. An attempt was now made to study plasticity more closely with this apparatus, and for a start the rate of extrusion as functions of the pressure applied and the temperature was studied. In order not to complicate matters, unmasticated raw rubber and raw rubber masticated for different lengths of time were used in the measurements, since in rubber mixtures the influence of the fillers and curatives may have a fundamental effect, as has already been shown in earlier work.

Whereas Marzetti weighed (in mg.) the quantity extruded and obtained the square root, I prefer to determine the volume extruded, since only in this way can the deformation be measured. Tables IX to XI show a number of these determinations, which were carried out with raw rubber of different degrees of milling.

TABLE IX

IA RIBBED SMOKED SHEET (20 KG. MASTICATED FOR 22 MINUTES)

Specific Gravity = 0.93

Temperature in ° C.	Pressure in Atmospheres							
	Mg.	5 Cu. Mm.	Mg.	10 Cu. Mm.	Mg.	15 Cu. Mm.	Mg.	20 Cu. Mm.
35	0	0	0	0	12	13	25	27
45	0	0	0	0	25	27	55	59
55	0	0	20	22	60	65	110	120
65	0	0	35	38	90	97	160	171
80	15	16	60	65	150	160	320	345

TABLE X

IA RIBBED SMOKED SHEET (20 KG. MASTICATED FOR 45 MINUTES)

Specific Gravity = 0.93

Temperature in ° C.	Pressure in Atmospheres							
	Mg.	5 Cu. Mm.	Mg.	10 Cu. Mm.	Mg.	15 Cu. Mm.	Mg.	20 Cu. Mm.
25	0	0	0	0	0	0	28	30
35	0	0	0	0	28	30	62	67
45	0	0	30	32	75	80	168	180
55	15	16	80	86	168	180	360	390
65	30	32	112	120	242	260	580	592
80	60	64	225	240	542	590	1265	1360

TABLE XI  
FIRST LATEX CREPE

Temperature in ° C.	Pressure in Atmospheres									
	5		10		15		20		30	
	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.
40	A <sup>a</sup>	..	..	..	..	..	..	..	..	..
	B	..	..	..	..	..	..	..	..	..
	C	..	..	..	..	..	..	530	570	990
	D	..	..	..	..	..	257	300	550	590
	E	..	..	..	..	..	635	680	2335	2500
	F	..	..	..	..	..	4300	4600	6300	6800
50	A	..	..	..	..	..	..	..	..	..
	B	..	..	..	..	..	..	55	60	150
	C	..	..	..	..	..	590	630	1150	1240
	D	..	..	..	..	..	600	650	1100	1200
	E	..	..	500	540	855	920	3600	3900	9300
	F	..	..	2100	2250	4500	4850	11300	12200	26700
60	A	..	..	..	..	..	..	..	..	..
	B	..	..	..	..	..	..	260	270	455
	C	..	..	..	160	170	400	435	1300	1400
	D	..	..	..	..	..	830	900	1950	2100
	E	..	..	875	940	2100	2250	5800	6250	14000
	F	..	..	3150	3400	10300	11100	31000	33500	22000
70	A	..	..	..	..	..	..	..	..	235
	B	..	..	..	..	..	..	210	225	610
	C	..	..	..	270	290	660	710	1900	2050
	D	..	..	..	660	710	1500	1620	3500	3800
	E	..	..	1075	1150	2450	2650	5900	6350	14000
	F	..	..	5100	5500	10300	11100	20200	22000	44000
80	A	..	..	..	..	..	..	195	205	540
	B	..	..	..	..	..	..	580	620	1185
	C	..	..	..	..	..	760	820	2600	2800
	D	..	..	..	930	1000	1500	1620	4500	4850
	E	740	800	1625	1760	4535	4900	9550	10200	22000
	F	2600	2800	4950	5300	16000	17200	23500	25500	47000
90	A	..	..	..	..	..	..	150	160	435
	B	..	..	..	..	..	..	930	1000	1500
	C	..	..	..	..	..	1500	1600	3600	3900
	D	..	..	500	540	900	970	2300	2500	5600
	E	1300	1400	2125	2300	5800	6250	11400	12200	29300
	F	1650	1780	10000	10800	21000	22500	33400	36000	91000

<sup>a</sup> See Table 13 for an explanation of the letters.

Since according to Marzetti the quantity extruded is proportional to the square of the pressure, the following relation must hold:

$$V/t = CP^2 \quad (1)$$

where  $V$  is the number of cubic millimeters extruded;  $t$  is the time (15 min.);  $C$  is a constant and  $P$  is the pressure in kg. per sq. cm. For example, if the value of  $C$  is calculated from Tables X and XI at 80° C., this equation gives the following values:

Pressure in atm.	5	10	15	20	30	40
$C$	2.6	2.4	2.6	3.4	4.3	4.7

Therefore  $C$  cannot be considered as a constant because it increases with increasing pressure.

In his book "Fluidity and Plasticity," Bingham<sup>12</sup> has the following equation for measuring plasticity according to the flow method:

$$V/t = C(P - p)(1 + \beta T) \quad (2)$$

where  $p$  is a constant,  $T$  is the temperature;  $\beta$  the temperature coefficient and the other factors are the same as in equation 1. With this equation and with the equation:

$$\frac{V_2}{V_1} = \frac{P_2 - p}{P_1 - p}$$

$p$  was first calculated as follows:

$$p = \frac{V_2(P_1 - V_1)P_2}{V_2 - V_1} \quad (3)$$

where  $V_2$  is the quantity extruded at  $P_2$  and  $V_1$  the quantity extruded at  $P_1$ , and where  $P_2$  is greater than  $P_1$ .

The value of  $P$  at different pressures and temperatures was obtained from a large number of determinations. These values are given in Table XII.

TABLE XII

 $p$ -VALUES

Tem- pera- ture in ° C. and X	From Table IX and X	Difference in Pressure in Atmospheres							
		5 to 10	10 to 15	15 to 20	20 to 30	30 to 40			
		From Table XI	From Tables IX and X	From Table XI	From Tables IX and X	From Table XI	From Tables IX and X	From Table XI	
35	..	...	...	10.4	..	..	..	..	..
	..	...	...	10.8	..	..	..	..	..
40	..	...	...	..	..	9.7	..	..	23.5
	..	...	...	..	..	16.0	..	..	17.8
	..	...	...	..	..	-9.0	..	17.9	16.2
45	..	...	6.7	10.8	..	..	..	..	..
	..	...	...	11.0	..	..	..	..	..
50	..	...	...	..	..	8.2	..	..	20.0
	..	...	2.9	..	13.6	..	13.7	24.2	9.2
	..	...	5.6	..	11.7	..	9.6	12.8	17.0
55	3.85	...	7.4	9.1	..	..	..	..	..
	..	...	5.3	10.7	..	..	..	..	..
60	..	...	...	..	..	14.2	..	..	24.9
	..	...	6.4	..	12.2	..	12.9	17.7	13.7
	..	...	7.8	..	11.8	12.5	15.4	19.2	23.8
65	3.4	...	6.8	8.4	..	..	..	..	..
	..	...	5.7	11.2	..	..	..	..	..
70	..	...	...	..	11.1	..	12.5	..	20.9
	..	...	6.1	..	11.4	..	12.6	24.8	17.5
	..	...	4.0	..	11.4	9.9	14.8	11.2	23.8
80	3.4	...	6.5	10.2	..	6.9	..	15.0	24.5
	3.2	0.8	6.6	7.2	11.0	10.4	..	12.6	20.6
	..	-6.0	...	7.7	..	4.7	15.8	10.0	21.2
90	..	...	...	3.7	..	12.0	..	13.0	24.7
	..	-2.8	...	7.1	..	9.8	..	13.6	13.4
	..	4.0	...	5.6	..	6.6	13.0	14.8	19.2

Here also  $p$  is not a constant if all the values are taken into consideration. There is, however, a certain constancy within a pressure range at different temperatures. If the values are examined more closely, an obviously regular increase of  $p$  with increasing pressure is found. Figures 7 to 9 show even better the continuous

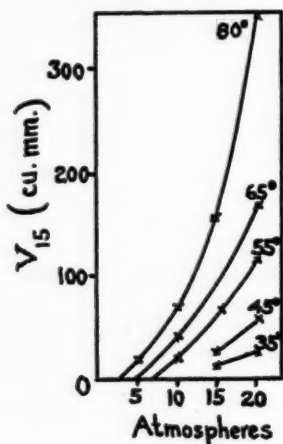


Figure 7

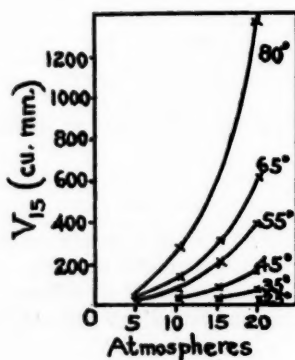


Figure 8

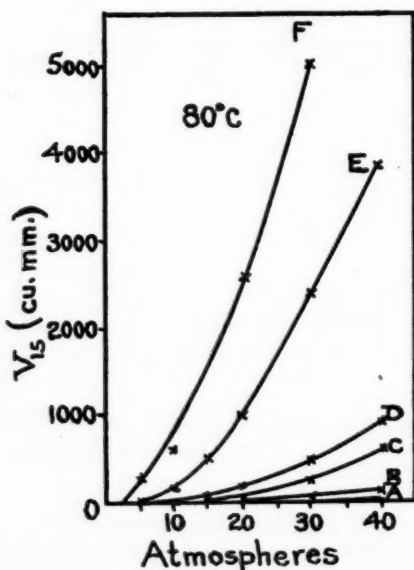


Figure 9

trend of the curves. What then is the significance of  $p$ ? If in Fig. 9, which shows graphically the values at 80° from Table XII, the curves are extended to the point of intersection with the abscissa, and if the pressures thus obtained are plotted against the "nerve" values of the raw rubber, determined by the capillary



method,<sup>13</sup> a straight line is obtained. It should be mentioned that the "nerve" values were obtained at room temperature, whereas the plasticity values were obtained at 80°.

Accordingly the "nerve" values have been recalculated on the basis of this temperature, using the coefficient 0.005 which has been given in earlier work.<sup>14</sup>

TABLE XIII  
FIRST LATEX CREPE

Sample	Pressure $p_0$	"Nerve" at	
		20°	80°
A unmastered	27	8300	5800
B 40 kg. of A, masticated 15 min.	21	5800	4100
C 10 kg. of B, masticated 20 min.	16	3775	2650
D 10 kg. of C, masticated 20 min.	11	2950	2050
E 5 kg. of D, masticated 10 min.	5	2300	1600
F 2.5 kg. of E, masticated 10 min.	2.5	1450	1050

This means therefore that the beginning of plastic flow, as well as its entire course in general, depends upon the "nerve" of the rubber. Before dealing with this more

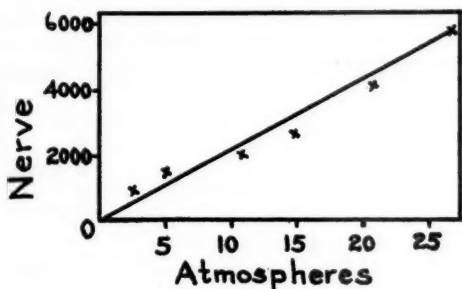


Figure 10

in detail the temperature coefficient  $\beta$  in equation (2) must be determined according to the following equation:

$$V_2 = V_1[1 + \beta(T_2 - T_1)] \quad (4)$$

where  $V_1$  is the quantity extruded at temperature  $T_1$  and  $V_2$  is the quantity extruded at temperature  $T_2$ , and where  $T_2$  is greater than  $T_1$ .

Table XIV and Fig. 11 give measurements at temperatures from 40° to 120° C. and at a pressure of 20 atmospheres, which make possible the determination of  $\beta$  by the formula:

$$\beta = \frac{V_2 - V_1}{V_1(T_2 - T_1)} \quad (5)$$

TABLE XIV  
1A RIBBED SMOKED SHEET (15 Kg.)

Time of Mastication	Quantity Extruded at 20 Atmospheres at Temperature in ° C.									
	40		60		80		100		120	
	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.
15 minutes	0	0	36	39	81	87	196	210	400	430
15 and 20 minutes	324	350	529	570	900	970	1850	2000	2300	2500

According to these data  $\beta \cong 5 \times 10^{-2}$ , which means that with an increase in temperature of about 20° C. the rate of extrusion becomes twice as fast.

Finally Table XV and Fig. 12 give plasticity-pressure curves for several mixtures. No. 1 is a mixture of 40 per cent rubber with whiting as a filler; No. 2 likewise contains 40 per cent of rubber and lamp black; No. 3 is a 40 per cent mixture with titanium oxide and whiting; No. 4 is an 80 per cent mixture, and finally No. 5 is an approximately 90 per cent mixture. As is seen, the character of the curves remains the same in comparison with those of raw rubber; the different fillers affect only the degree of the plasticity.

TABLE XV  
MIXTURES (TESTED AT 80° C.)

Expt.	Specific gravity	Pressure in Atmospheres											
		5		10		15		20		30		40	
		Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.	Mg.	Cu. Mm.
1	1.52	0	0	105	70	320	210	1600	1050	5300	3500	14800	9800
2	1.51	0	0	0	0	575	380	1500	1000	4450	3000	16350	10800
3	1.58	0	0	625	395	1730	1100	3900	2450	25500	16000	54200	34500
4	1.06	0	0	245	230	1500	1400	2700	2500	8200	7700	14500	13500
5	0.99	0	0	500	510	2000	2000	3600	3650	9700	9800	21200	21500

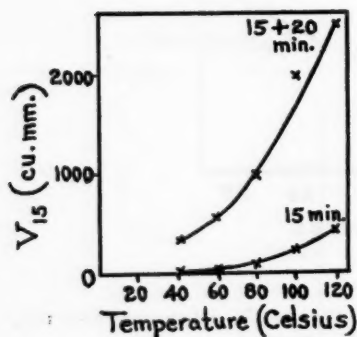


Figure 11

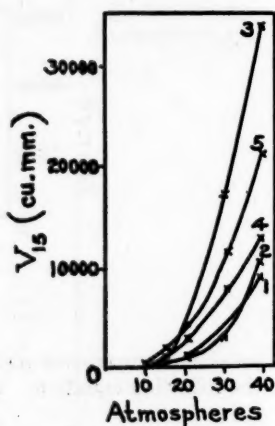


Figure 12

What is to be thought of the phenomenon in general? As has been emphasized in earlier work,<sup>15</sup> the concepts of "nerve" and plasticity must be sharply distinguished at all times. In that work it was pointed out that plasticity must be understood to involve the displacement of micelles, whereby these micelles still remain within their mutual spheres of action. On the other hand by "nerve" is meant the cohesion of the micelles. On this basis it is possible to interpret the experimental results. Plastic deformation occurs at low pressures, whereas only at higher pressures, from 20 to 30 atmospheres, varying with the degree of mastication of the rubber, does rupture of the micelles take place. Let us consider Fig. 10 once more. If the curve is extended to the point of intersection with the abscissa, it will be found that it ends at the zero point. Of course account must be taken of the fact that the measurement of the pressure involves comparatively large errors, so that it is not possible to say whether or not the straight line cuts the abscissa axis somewhat beyond the zero point. In any case, however, the experiments at least show that the true plasticity of unmasticated raw rubber is only very

small and that only when the milling has ruptured part of the micelles can plastic deformation take place at low pressures. This is seen in the plateau section of the curves, only the steep rise indicates a rupture of the remaining micelle groups. Accordingly  $p$  (Equation 3) represents the algebraic sum of "nerve" and plasticity when the two values have opposite signs. In other words:

$$p = \text{"nerve"} - \text{plasticity}$$

In other words, the greater the "nerve" the smaller is the quantity extruded, and the greater the plasticity the greater is the quantity extruded. At low pressures or where the "nerve" is partially destroyed, the plasticity value still plays a part in comparison with that of the "nerve" value in the determination of  $p$ , whereas at higher pressures it may be disregarded and the  $p$  value is then calculated only from the "nerve."

What forces act on the rubber during its milling in practice? The following calculation<sup>16</sup> will serve to answer this question. If a piece of rubber is squeezed between two rolls rotating in opposite directions, the work done by the system is expressed by the pressure on the roll bearings. This is  $\mu K v$ , where  $K$  is the pressure on the rolls,  $\mu$  the coefficient of friction, and  $v$  the distance traveled by a point on the circumference of the axis per second. This work is measured by the quantity of electricity consumed, and therefore when the system of measurement is expressed in  $\mu K v$  with a three-phase alternating current it is:

$$\mu K v = \frac{EI\sqrt{3}(\cos \varphi)101.98}{1000} \quad (6)$$

where  $E$  is the voltage,  $I$  the current strength and  $\cos \varphi$  is the power factor.

From this it follows that:

$$K = \frac{EI\sqrt{3}(\cos \varphi)101.98}{\mu v \cdot 1000} \quad (7)$$

If we now consider the energy consumed when running idle, and if the values obtained in practice are:

$$\begin{aligned} E &= 380 \text{ volts; } \cos \varphi_1 = 0.8; n = \text{revolutions per second} = 0.275; \\ I_1 &= 70 \text{ amperes; } \cos \varphi_1 = 0.1; 2r_1 = \text{diameter of the axis} = 0.310 \text{ m.;} \\ I_0 &= 50 \text{ amperes; } v = 2r_1 n = 0.266 \text{ m.} \end{aligned}$$

then

$$K = \frac{E\sqrt{3}(I_1 \cos \varphi_1 - I_0 \cos \varphi_0)101.98}{\mu v \cdot 1000} = 159701 \text{ kg.}$$

Since the pressure is divided between both rolls, the values obtained should be divided by two, since the pressure and resistance are the same. The pressure is distributed over the entire length of the rolls, and if we assume a roll 150-cm. long and 50 cm. in diameter with a layer of rubber 0.6 cm. thick, and a bank of 5 cm., then its height  $h$  can be calculated with the aid of Fig. 13.

$$r = 25 \text{ cm.; } AE = 5 \text{ cm.; } CD = 0.6 \text{ cm.}$$

$$h^2 = r^2 - AC^2 = r^2 - \left(r - \frac{AE}{2} - \frac{CD}{2}\right)^2 = 105 \text{ sq. cm.}$$

therefore

$$h = 10.2 \text{ cm.}$$

The pressure  $K$  is therefore distributed upon a surface  $F = 150 \times 10.2 = 1530$  sq. cm., and the pressure per sq. cm. is accordingly 51 kg. Average values have been used which naturally may be many times greater during the mastication of raw rubber. However, it is seen from the order of magnitude that these pressures would be the same as with the Marzetti plastometer.

It still remains to be seen how the other types of apparatus which have become known through the literature answer the requirements which are demanded of them, both from a scientific and from a practical point of view. Griffith<sup>17</sup> works upon the same principle as Marzetti, except in the former case the pressure is obtained not by compressed air but by a load of 1000 lbs. or 453.6 kg. The discharge nozzle is removable, and nozzles of diameters of 1.6 to 4 mm. can be used, depending upon the softness of the rubber. To carry out the test, a cylinder one inch (2.5 cm.) in diameter and 2.25 inches (5.6 cm.) long is cut out, and is preheated in a thermostat. After one hour it is placed in the pressure chamber, exposed two minutes at full pressure with the nozzle closed, and then put under pressure until the piston has descended about two centimeters. The time required in minutes gives a measure of the plasticity of the rubber.

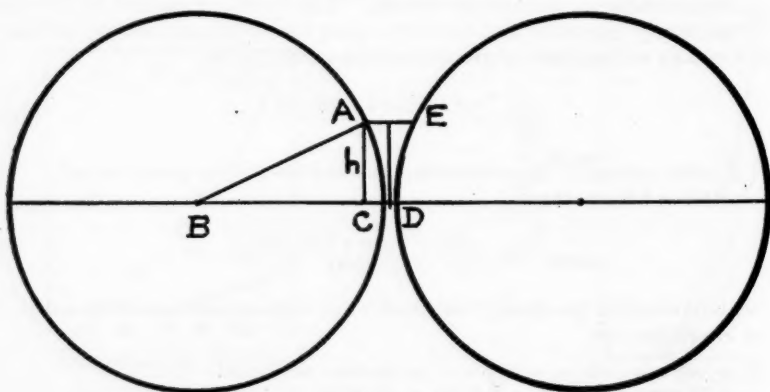


Figure 13

Besides the higher pressure (approximately 90 kg. per sq. cm.) the chief difference between this and the Marzetti plastometer is the manner of measurement. Instead of determining the quantity extruded, the descent of the piston is measured. According to my experience with this apparatus, this in itself seems to be its fault. First of all only the total compressibility of the mass is measured, which though it may depend upon the plasticity, varies greatly according to the quantity of air which is milled into the particular rubber. Then again in practice it is very seldom that it is possible to avoid a sliding of the rubber between the wall and the piston, and through the resulting increase in friction this interferes with the steady descent of the piston. In every case I have observed exactly this sort of jerky motion. Last of all, it would be advantageous to avoid extrusion into water, since even the smallest quantity of water which penetrates into the pressure chamber or even only into the nozzle vitiates the results, for it is a well-known fact that water acts as a plasticizing agent.

In America the apparatus which is mostly used is that first described by Williams.<sup>18</sup> It consists of two metal plates of which the upper one is loaded with a weight of

5 kilograms, and can be moved up and down parallel to the lower plate. Between these two plates Williams lays the rubber to be measured in the form of a sphere or a cylinder of 2-cc. capacity, places the whole apparatus in a thermostat at 80 or 100° C., and releases the upper plate so that the test piece is subjected to the load. The rate at which the upper plate descends, i. e., the diminution in the thickness of the rubber, is observed by the aid of a scale, and is plotted graphically. Since according to Williams the curve conforms to the equation  $K = yx^n$ , where  $y$  is the thickness of the sample,  $x$  the time in minutes,  $n$  a constant and  $K$  the plasticity factor, the plasticity of the substance is thus obtained. De Vries,<sup>19</sup> who also worked with the Williams plastometer, proved that the formula is only approximately correct. The values plotted on a logarithmic scale do not lie exactly on a straight line, but instead the curve bends somewhat toward the time axis. He therefore determined the plasticity by measuring the thickness ( $D_{30}$ ) after 30 minutes and also determined the bend in the curve, the  $n$  in the Williams equation, from the difference in the thickness ( $D_{25} - D_{35}$ ) after 25 and after 35 minutes.

In this connection, Van Rossem<sup>20</sup> has already called attention to the fact that with this instrument the various relations are not so simple as appears at first glance. In the first place it must be remembered that the pressure on a unit surface decreases continuously during the time of the experiment. This in itself gives an explanation of the form of the Williams curve, which approaches asymptotic to the abscissa. Van Rossem and de Visser<sup>21</sup> before him attempted to overcome this fault by attaching a raised rim on the bed plate so that the weight at all times presses on a constant area. De Vries<sup>22</sup> found that this modification, at least with unmasticated rubber, led to erratic and confusing results because the rubber ring which presses between the rim and the upper plate has so little plasticity that it prevents any further flow of the rubber. Van Rossem calls attention to another fault. If the test sample is unloaded after the experiment, it is noticed that there is a tendency to resume its original form, with a resulting increase in height. In other words, not only the permanent, but also the elastic deformation is measured, and in order to obtain correct values of the plasticity it would be necessary to subtract the elastic recovery from the thickness  $D_{30}$  or  $y$  in the Williams formula. In an exhaustive investigation of this plastometer, Scott<sup>23</sup> also came to the conclusion that the ordinary method of determining plasticity by measuring the thickness after a definite time of compression is open to objection. Moreover it is also impossible to measure the exact quantity of air within the rubber. The chief objection against this apparatus, however, is that the pressure (6.3 kg. per sq. cm.) is much too small compared to the forces which are encountered in practice. In this connection the trend of the curves in Figs. 7 to 9 should be compared. Karrer<sup>10</sup> followed the same principle as Williams, only he avoided this fault. He used cylindrically shaped test pieces 1 cm. in diameter and 1 cm. high, and pressed them together by means of a spring. After 5 seconds they were released and the decrease in height was measured. The plasticity  $P$  is then represented by the formula developed by Karrer:

$$P = \frac{K(h - h_2)}{Fh} \quad (8)$$

where  $K$  is a constant;  $h$  the original height,  $h_2$  the height after release, and  $F$  the force applied.

The force amounted to 0.1 to 4 kg. and is therefore too small for comparison with the conditions in practice, as has already been seen. From a theoretical point of view, however, the work is very interesting since the attempt was made to define the idea of plasticity and to distinguish between plasticity and "nerve," upon which



I have always laid stress. Unfortunately I do not know this apparatus from my own experience, so that it is impossible for me to pass final judgment upon it. Here too, however, the influence of the air in the rubber is a source of noticeable trouble.

In conclusion it may be said that the Marzetti plastometer seems to give the most certain indication of the behavior of raw rubber or of rubber mixtures on a practical scale, since it approaches most closely practical conditions. During seven years' work with this apparatus I have repeatedly found that the results agree well with practical mill, calender, and tubing machine operations, and in a great many cases improvements in mixing can be made on the basis of plastometer measurements. The parallel-plate plastometer is often found wanting in such cases. The Karrer apparatus on the other hand seems to be very interesting from a theoretical point of view, since perhaps it will make it possible to measure the absolute plasticity of rubber as well as to obtain a closer insight into the concept of "nerve," and in this way to compare the method of Greinert and Behre with that of Berggren.<sup>24</sup>

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- <sup>2</sup> *Z. techn. Physik*, **8**, 326 (1930).
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- <sup>4</sup> *Inst. Rubber Ind. Trans.*, **1**, 308 (1926).
- <sup>5</sup> Greinert and Behre, *Kautschuk*, **2**, 207 (1926).
- <sup>6</sup> See Note 5.
- <sup>7</sup> *Kolloid-Z.*, **57**, 67 (1931).
- <sup>8</sup> Behre, *Kautschuk*, **2**, 280 (1926).
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- <sup>13</sup> Greinert and Behre, *Kautschuk*, **2**, 63 (1926).
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- <sup>16</sup> I thank Dipl.-Ing. Kunze for this suggestion.
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# The Surface Properties of Rubber

E. Vellinger

It is known that the properties of rubber depend in large measure upon the nature of the ingredients which are compounded with it. Certain facts seem to show the enormous effect on the mechanical properties of rubber of surface forces which

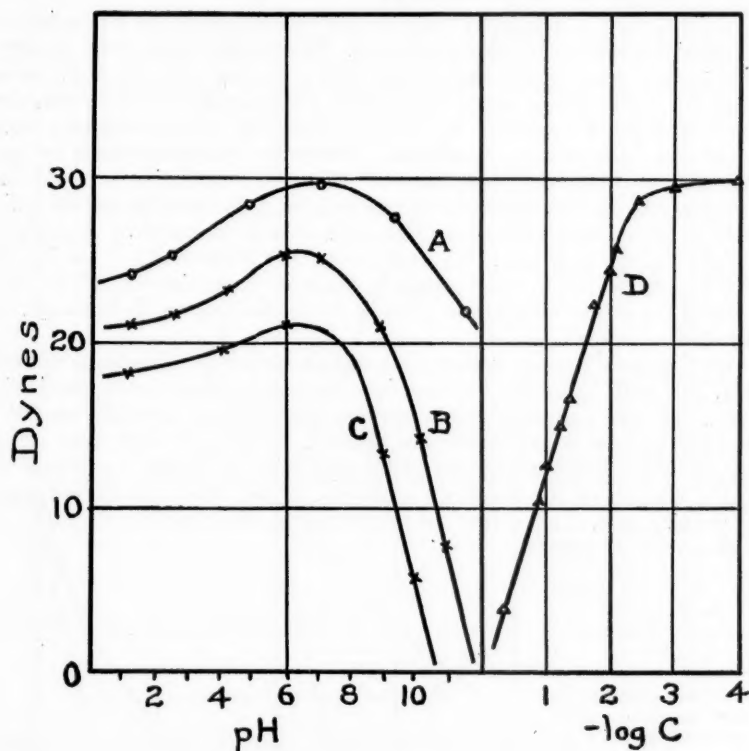


Figure 1

Figure 2

Figure 1—Curve of the Interfacial Tension, as a Function of the pH Value of the Solvent (A), of a 0.3% Benzene Solution of Raw Rubber (B), and of a 0.02% Benzene Solution of Resin (C)

Figure 2—Curve of the Interfacial Tension of Benzene Solutions of Resin as a Function of the Negative Logarithm of the Concentration (in Grams per 100 Cc.)

intervene between the rubber and the filler. In order to study the influence of this factor, the surface activity of the rubber was investigated in the present work. This activity was determined by measuring the lowering of the interfacial tension between a benzene solution of rubber and aqueous solutions of electrolytes by the tensiometer method of le Comte du Noüy, following a technique already described by the author and Weiss for measuring the interfacial tension of mineral oils.

Under these conditions, the curve of the interfacial tension as a function of the  $p_H$  of aqueous solutions has a characteristic form. The extremity of the curve, corresponding to high  $p_H$  values, descends sharply toward the axis of the abscissae (Fig. 1). The question might then be asked what is the relative activity of the different components which, under normal conditions, enter into the composition of the rubber. The surface activity of pure rubber with certain of its components removed by acetone extraction is equal or inferior to that of pure benzene. Purified, in this way, rubber is rapidly altered by oxidation. The alteration products are very active, and it is difficult to obtain an absolutely inactive product. On the contrary the acetone extract is enormously active. A solution of 1 mg. of resin in 100 cc. of benzene can be easily detected.

Figure 2 shows the interfacial tension of a benzene solution as a function of the concentration when  $p_H$  is approximately 6. The tension drops very rapidly and approaches zero for concentrations of the order of one per cent. It should be noted that the interfacial tension is a linear function of the logarithm of the concentration of the resin between 1 and 0.01 per cent. The acetone extract contains a series of compounds of different surface activities. Besides free resin acids, there are present saponifiable products, the proportions of which vary according to the origin of the rubber. At high  $p_H$  values, these products have considerable surface activity, a result of the neutralization of the free acids or acids liberated by saponification, which act through their ions. We have shown that the lowering of the interfacial tension by active acids is much greater in the case of the dissociated form than in the case of the undissociated form (*Compte Rendu du Congress du Graissage, Strasbourg 1931*, page 354).

There is a close analogy between the surface properties of mineral oils and of rubber. In both cases the hydrocarbons suitably purified have practically no activity. On the contrary, certain components which are normally present with these hydrocarbons have considerable activity. Finally, in both cases oxidation of the pure hydrocarbons results in the formation of active substances which probably include all the stages of oxidation between the hydrocarbon and the corresponding acid. One is thus led to attribute to the resin the chief role in the surface activity of rubber.

# The Surface Affinity of Rubber for a Filler

E. Vellinger

It is known that there is a relation between the mechanical properties of rubber and the nature of the filler or pigment which is incorporated in it. It has been

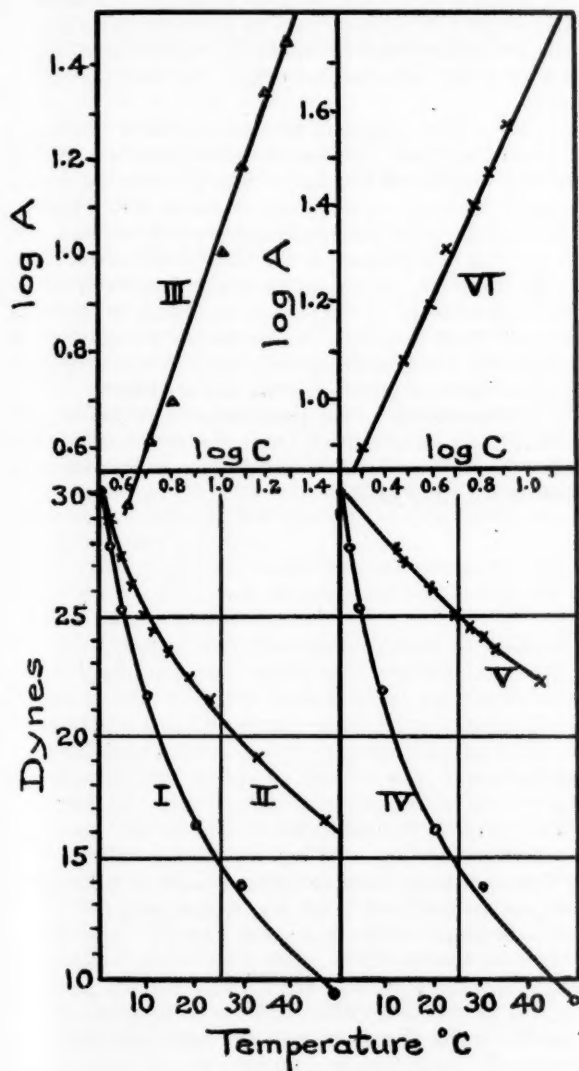


Figure 1—Curve of the Interfacial Tension of Benzene Solutions of Resin as a Function of the Concentration (in mg. per 100 cc.) in the Absence of Rubber (I); in the Presence of Rubber (II); in the Absence of Gas Black (IV); and in the Presence of Gas Black (V). Adsorption of Resin by Rubber (III) and by Gas Black (VI). Logarithmic Expression of the Adsorption Isotherm of Freundlich (A is the Quantity of Resin Adsorbed and C the Concentration of the Solution).

proved that certain fillers have the property of improving considerably the characteristic mechanical properties of rubber. Thus zinc oxide has proved to be a better reinforcing agent than some substances with a finer particle size. Lithopone, with a fineness which is of the same order of magnitude as that of zinc oxide, has no reinforcing action whatever. Gas black has the most powerful action known. Moreover all reinforcing fillers are very good absorbents. On the contrary inert fillers are of little account from this point of view. The phenomena of adsorption seem then to play an important part in the reinforcing action of fillers, and consequently substances with strong surface activity are adsorbed by these fillers.

It has been shown (see preceding article) that the activity of pure rubber, freed from its resinous components, is very low, if it has any activity at all. On the other hand, the resins extracted from rubber by acetone have an extraordinary activity. For this reason it may be asked whether or not the resins play an effective part in the reinforcing action because of a very great surface affinity for both the rubber and the filler at the same time.

In fact, experiments have shown that resins are adsorbed by both substances to an equal degree. If the interfacial tension of benzene solutions of the resins is determined both in the presence and in the absence of fillers, it can be proved that the presence of adsorbing substances causes a high elevation of the tension. This makes it appear as if part of the resin was eliminated from the solution (see diagram). It may be supposed that this increase in the interfacial tension corresponds to the quantity of resin adsorbed. It is possible to calculate the quantity of the resin adsorbed and the concentration of the benzene solution corresponding to this tension. The logarithms of these quantities can be expressed in the form of a law which approximates very well the logarithmic expression of the adsorption isotherm of Freundlich. The same facts are observed in the case of rubber.

It is known that the resin is indispensable to the preparation of rubber of good quality. It seems therefore that its role is to activate the rubber hydrocarbons and to bring about a surface union (*liaison*) between the active filler on the one hand and the slightly active rubber on the other hand.



# The Solvation of Rubber Sols

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The purpose of this investigation was to get some idea of the role played by solvation in organo sols. However, we wish to state first that we do not bind ourselves to a special theory. Accordingly we give these systems the name sols simply because we cannot speak of them without giving them a name. It may be that the name "solution" is a better one, but for our purpose it does not make the slightest difference whether the rubber is dispersed in the medium as molecules or as aggregates of molecules. Hence we do not want to discuss the molecular structure of the rubber particles in detail.

There are many methods of measuring the degree of solvation, but they almost never give quantitatively the same results, which cannot be expected at any rate. Previous investigators have used the greatest part of these methods with more or less success.

The best known are the investigations of Posnjak<sup>1</sup> on the swelling-pressure of rubber in organic solvents.

Furthermore, many investigators have measured the viscosity of rubber sols. But while it is likely that the law of Poiseuille does not hold, and that these sols are plastic, it will be very difficult to interpret the values so obtained in the right way. Recently Stamberger<sup>2</sup> measured the vapor pressure of rubber sols and got a good agreement with Posnjak's values. However, Stamberger did not extend his measurements to concentrations between 67 per cent and 100 per cent rubber, probably because he was looking for this agreement only.

We needed a method which would permit measurements at every concentration and would give in some way a value for the solvation. We cannot mention here all the objections and disadvantages of other methods. The method used here was that of vapor pressure.

A relative method cannot be used because of lack of material for comparison. Using a direct method one has to be very careful, since the dissolved air may make the results very inaccurate.

It was found that the simple apparatus designed by Smith and Menzies<sup>3</sup> was very useful and gives satisfactory results if one wants to have a general view of the phenomena. Yet this method is not sufficiently accurate for dilute sols, so that practically it is of use only in the range between the rubber concentrations corresponding to relative vapor pressures between 97 per cent and 5 per cent.

Mercury was used in the small U-tube connected directly with the bottle containing the sol, other liquids being impossible, as they give solutions with the organic vapors. So we had to take four cathetometer readings for every measurement, two on the manometer and two on the mercury levels in the U-tube. However, the error in these readings is small compared with the other errors. We might mention here that, to get rid of the dissolved air, the method described below is sufficient: A small amount of rubber (approximately 500 mg.) is weighed in the container, and roughly 20 cc. of the solvent are added. After the rubber has dissolved, the container is fixed to the apparatus and the contents evaporated till only about 10 cc. are left. After some hours, this is repeated until roughly 6 cc. are left, and then the first reading is taken. The container being weighed, one can make a second measurement, and so on. It seems to take a long time before the

air redissolves in the sol. The results so obtained are easily reproducible with different sols. The values obtained for the pure solvents are in good agreement with the values found in the literature.

The time necessary for reaching equilibrium varies with the amount of rubber, solvent, concentration, and temperature between 10 minutes and some hours. Especially at the higher concentrations however, equilibrium is reached very soon.

For these investigations were used:

- (a) An ordinary sample of sole crepe rubber;
- (b) Purified samples.

To purify the crude rubber the method described by Pummerer, Andriessen and Gündel<sup>4</sup> was used. They call this rubber sol rubber. But Whitby<sup>5</sup> showed that there is no sharp boundary between sol and gel rubber, and that the amount of gel rubber is a function of different circumstances. Yet Pummerer's method is very useful for obtaining a N-free rubber easily.

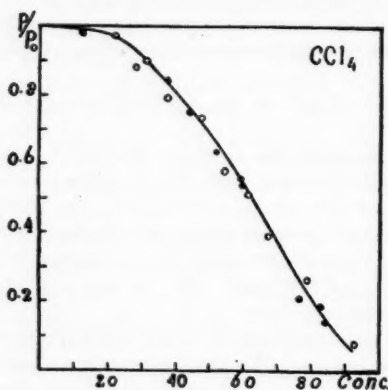


Figure 1

● = Crude rubber  
○ = Purified rubber

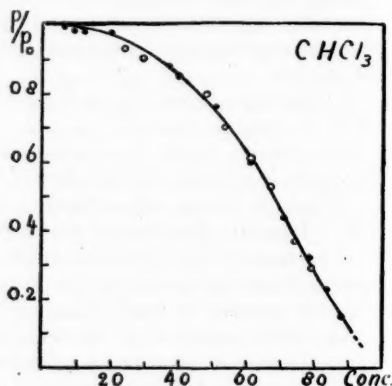


Figure 2

● = Crude rubber  
○ = Purified rubber

According to the United States Bureau of Standards<sup>6</sup> very pure rubber can be distilled in vacuum. If this is possible with pure rubber, it might also be possible with crude rubber. Attempts in this direction failed entirely, however.

In the first place we measured the vapor pressure-concentration curves in chloroform, carbon tetrachloride and benzene for crude and purified rubber. As one can see from Tables I-VI and Figs. 1-3, there is hardly any difference in the behavior of crude and pure rubber according to the vapor pressure lowering. This lowering up to concentrations of 15-20 per cent is very small. This caused Stamberger<sup>7</sup> to calculate a value for the highest solvation value possible in a given solvent by assuming that no free solvent is left when the curve goes down. However, this is very questionable, for Stamberger assumes this point to be at 20 per cent concentration of rubber. If, however, the osmotic pressure is plotted against the concentration,<sup>7</sup> as Kroepelin and Brumshagen<sup>8</sup> did, one gets a curve already bending at 1 per cent, and so the solvation would be 20 times as much. Meyer and Mark<sup>9</sup> calculated in the same way that the amount of liquid taken up was 20-40 times the amount of rubber. One obviously cannot say where the solvate layers of the particles end, and at which concentration all the liquid is bound. The curve is

entirely smooth, and every calculation based on some fictitious bending point is very questionable.

In the case of the system rubber-benzene we got certain peculiarities, due to non-equilibrium. If one uses a sol which is only made the day before, one gets a curve which apparently shows a range of liquid-liquid separation (Fig. 4). The position of this range is dependent on the age of the sol and its former history, as can be shown by comparing the different curves. This looks similar to the case of the vapor pressure curve of a  $\text{SiO}_2$  gel, as investigated by van Bemmelen.<sup>10</sup> However, there is one difference: the whole curve is reversible. If, coming from the more dilute systems, one passes first the range of separation entirely and then goes back by adding benzene, one gets values on the same curve. The whole phenomenon has disappeared after four days, and the curve then obtained coincides with that of a three months' old sol.

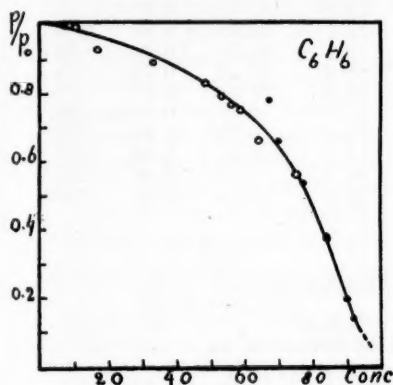


Figure 3

● = Crude rubber  
○ = Purified rubber

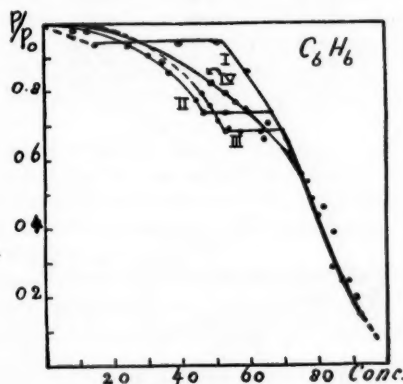


Figure 4

Curves I, II, and III sols. freshly prepared.  
Curve IV. Coinciding curves for a 6 days' old  
and a 3 months' old sol.

TABLE I

CRUDE RUBBER- $\text{CCl}_4$ ;  $T = 35^\circ$

G. Rubber 100 G. Sol	$p$ (Cm. Hg)	$\frac{p}{p_0}$
0	16.34	1
12.1	16.15	0.99
37.6	13.79	0.84
44.0	12.30	0.75
51.8	10.52	0.64
58.6	9.32	0.56
59.8	8.87	0.54
75.7	3.43	0.21
82.6	3.06	0.19
83.8	2.34	0.14

TABLE II

CRUDE RUBBER- $\text{CHCl}_3$ ;  $T = 35^\circ$

G. Rubber 100 G. Sol	$p$ (Cm. Hg)	$\frac{p}{p_0}$
0	28.19	1
6.0	27.82	0.99
9.1	27.68	0.98
12.2	27.59	0.98
20.3	27.57	0.98
37.1	24.93	0.88
50.7	21.52	0.76
61.1	16.92	0.60
70.8	12.50	0.44
79.1	9.00	0.32
83.9	6.66	0.23
88.2	4.86	0.15

In a new sol, any increase of opalescence in the range of separation could not be seen. This cannot be expected, since the refractive indices of the two phases must be very near to each other, owing to the fact that the refractive indices of rubber and benzene are already so near to each other.

From the change in the relative vapor-pressure with temperature it is possible to calculate the heat of dilution thermodynamically. Kroepelin and Brumshagen<sup>8</sup> made measurements of the osmotic pressure at different temperatures from the same point of view and found that the heat of dilution in benzene was extremely small, *i. e.*, less than 0.001 calorie per gram of rubber. Boström<sup>11</sup> found by direct calorimetric measurement a value of 1.6 calorie per gram of rubber swelling in benzene.

TABLE III

CRUDE RUBBER— $C_6H_6$ ;  $T = 35^\circ$ 

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$
0	14.35	1
67.4	11.31	0.78
70.1	9.58	0.66
77.3	8.06	0.54
83.8	5.54	0.38
89.7	2.70	0.19
92.0	2.03	0.14

TABLE IV

PURIFIED RUBBER— $CCl_4$ ;  $T = 35^\circ$ 

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$	$P$ (At.)
0	16.34	1	
12.7	16.04	0.98	
22.2	16.10	0.98	
27.7	14.32	0.88	30
31.1	14.75	0.90	25
35.3	12.95	0.79	54
47.3	12.10	0.74	70
53.7	9.47	0.58	126
61.3	8.29	0.51	156
67.3	6.35	0.39	217
78.7	4.19	0.26	310
92.4	1.34	0.08	700

TABLE V

PURIFIED RUBBER— $CHCl_3$ ;  $T = 35^\circ$ 

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$	$P$ (At.)
0	28.19	1	
11.8	28.07	1	
24.1	26.14	0.93	
29.7	25.36	0.90	30
40.0	24.04	0.85	45
48.2	22.44	0.80	62
53.2	19.68	0.70	100
61.3	17.43	0.62	133
67.3	15.09	0.53	175
73.9	10.25	0.36	285
79.3	8.18	0.29	345

TABLE VI

PURIFIED RUBBER— $C_6H_6$ ;  $T = 35^\circ$   
6 Days' Old Sol

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$	$P$ (At.)
0	14.35	1	
7.45	14.33	1.00	
10.5	14.30	1.00	
17.4	13.50	0.93	20
33.5	12.86	0.89	30
48.7	12.00	0.83	47
53.3	11.40	0.79	60
56.4	11.06	0.76	69
59.0	10.80	0.75	72
59.7	10.55	0.73	79
64.4	9.54	0.66	105
75.6	8.19	0.56	146
84.5	5.51	0.38	240

Unfortunately the degree of accuracy was far from sufficient to measure those small values in this indirect way. It is of no use to give the result of our experiments in detail. It may be observed that the relative vapor pressures remain constant within 2 per cent at temperatures between  $25^\circ$  and  $45^\circ$ . That the heat of dilution cannot amount to 25 calories is the only and not very remarkable conclusion which can be drawn. As the method of the osmotic pressure measurement is much more sensitive, Kroepelin and Brumshagen were able to find an effect by working at different temperatures. But just this sensitivity is the reason that the concentrations which can be used are only small ones.

Accordingly, one cannot consider these systems as ideal solutions. For if one calculates the molecular weight from the obtained data, one gets values varying between 300 and 600, even with the assumption of a constant amount of solvent inactivated per gram of rubber.

Thermodynamically, no further information can be obtained from these figures. From the kinetic point of view we can do something more. From the vapor pressure curve we can calculate the osmotic pressure curves, using the equation:

$$P = - \frac{RT}{Mv} \ln \frac{p}{p_0}$$

Now the osmotic pressure is due to two factors, the number of particles present and the solvation of these particles.

The solvation comes in, when the solute molecules are so close to each other that all the solvent is more or less bound. Theoretically all the solvent will always be bound, but in more dilute sols the binding of the least attracted solvent molecules will be so weak that no influence of the solvation on the osmotic pressure may be expected. How dilute a sol or a solution has to be depends on solute and solvent. Here in the case of rubber in an organic medium, it is known that even in very dilute sols there is an influence of the solvation on the osmotic pressure. This can be seen from the figures obtained by Kroepelin and Brumshagen, who found that the osmotic pressure of a 0.5 per cent sol still varied with temperature, but not in the ratio as might be expected from the van't Hoff equation. Hence there is still a heat of dilution, though a very small one.

Undoubtedly the particle size or the molecular weight is large in the cases discussed. The osmotic pressure therefore is chiefly due to the solvation of the particles. This means that one measures chiefly the swelling tendency of the particles. These particles can be as already considered in the introduction, either molecules, aggregates, or even aggregated aggregates, that is to say, a gel.

In Tables IV-IX are compiled the calculated values for the osmotic pressure  $P$  amounting to enormous values at high rubber concentrations. One cannot take into account the values for the low rubber concentrations, as the error can amount to several hundred per cent here, because  $\log \frac{p}{p_0}$  is so small in these concentrations.

An error of 1 per cent in  $\frac{p}{p_0}$  gives an error of 50 per cent in  $\log \frac{p}{p_0}$ . With decreasing value of  $\frac{p}{p_0}$  the magnitude of this error decreases rapidly.

It is a well known fact that in certain solvents one gets an unlimited swelling of the rubber, in others only a limited swelling. Now it was interesting to see how the vapor or osmotic pressure curve would be for a solvent which gives only limited swelling. These curves were estimated for acetone, methyl and ethyl alcohol (Tables VII, VIII, IX, Fig. 5). They were very easy to measure; even for values of  $\frac{p}{p_0}$  near 1 we got good results with a very small experimental error, and reproducible smooth curves.

They have the same shape as the other curves, but only in the very high rubber concentrations.

An analogy exists in the ordinary binary systems with two components with lower molecular weights, showing a range of separation with one layer containing practically only one component.

Here as well the amount of rubber in the upper layer can be neglected. One sees from these curves that the first amount of solvent is bound strongly, but that the binding capacity gradually diminishes to zero. The same phenomenon must occur in the cases of rubber-benzene, etc., except that the amount of solvent bound is much more, for even in a 0.5 per cent sol saturation of the particles is not



yet reached. This leads to the suggestion that there is only a gradual difference in the behavior of acetone and benzene. A liquid-liquid separation would then occur in the system rubber-benzene in a range between 0 per cent and maximal 0.5 per cent. On the other hand, one cannot expect, if there really is such a range of separation in these diluted sols, that the rubber containing phase will settle down. This phase will show practically no difference in density and surface tension with the other one, the pure benzene. So it remains suspended, and gives the system an osmotic pressure against the medium.

TABLE VII

PURIFIED RUBBER—METHYL ALCOHOL;  
 $T = 35^\circ$

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$	P (At.)
0	19.25	1	
88.3	19.23	1.00	
88.9	19.07	0.99	
95.5	18.95	0.98	8
96.8	17.33	0.90	60
96.8	17.05	0.89	64
99.2	14.33	0.74	170
99.7	8.29	0.43	470

TABLE VIII

PURIFIED RUBBER—ETHYL ALCOHOL;  
 $T = 35^\circ$

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$	P (At.)
0	9.15	1	
79.3	9.10	1.00	
91.0	8.67	0.95	20
91.7	8.50	0.93	28
98.8	7.03	0.77	101
99.2	5.25	0.57	215

TABLE IX

PURIFIED RUBBER—ACETONE;  $T = 35^\circ$

G. Rubber 100 G. Sol	$\frac{p}{p_0}$ (Cm. Hg)	$\frac{p}{p_0}$	P (At.)
0	33.65	1	
72.6	33.60	1.00	
80.4	33.05	0.98	
83.6	32.53	0.97	10
84.8	32.38	0.96	12
85.6	31.90	0.95	16
87.1	30.85	0.91	29
88.4	29.92	0.89	35
92.9	22.50	0.67	122
97.0	13.02	0.39	290
97.9	7.63	0.23	450

One can thus speak of the ideal volume of a particle. That is to say, the particle tends to bind a certain volume of solvent, and we call the volume of a particle with all the solvent it can bind its ideal volume. It may be that this ideal volume is a fictitious one, because the solvate layer has a diffuse boundary between it and the medium.

If the total ideal volume of the particles equals the volume of the sol or is larger, the sol will be stable, if not it will settle down, except in the cases where the difference in density between solvated particle and medium is not sufficient.

It is obvious that the ideal volume of a particle in benzene can be decreased by adding acetone, etc., for the final state, if an infinite amount of acetone is added, is that with the ideal volume of the particles in acetone. So by adding acetone one comes in a dilute sol to a point where the ideal volume is decreased so far that the difference in density is sufficient to give coacervation, or in a more concentrated sol so far that the ideal volume is smaller than the sol volume. We did not take into account here the mutual attraction of the sol particles, a complicating factor.

According to Fig. 5, acetone has the largest ideal volume, then ethyl alcohol, then methyl alcohol. One may expect that we need therefore the largest amount of acetone to give coacervation in a benzene sol. We measured this degree of coacervation by the light-scattering of dilute sols. Hence the difference of refractive index between particle and medium comes in. Nevertheless, the curves of Fig. 6 show that methyl alcohol has the strongest coacervating capacity. The difference between ethyl alcohol and acetone is doubtful. Probably the factor already mentioned comes in. An experiment like this can never be a strong support for any theory.

These measurements were done with the light-scattering apparatus of Krishnamurti.<sup>12</sup> They were extended to the homologs of the alcohol series. With increasing C number the coacervating capacity decreases, or the ideal volume of rubber in these solvents increases.

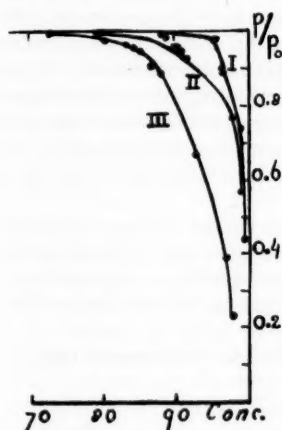


Figure 5

- I = Purified rubber and methyl alcohol  
 II = Purified rubber and ethyl alcohol  
 III = Purified rubber and acetone

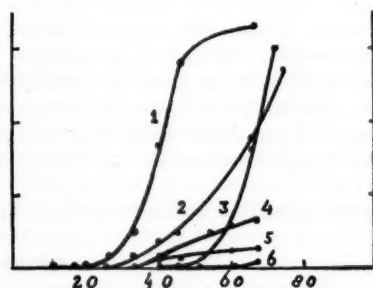


Figure 6

- Abaxis. Alcohol in per cent  
 Ord. Intensity of scattered light  
 Curve 1 = Methyl alcohol  
 Curve 2 = Ethyl alcohol  
 Curve 3 = Acetone  
 Curve 4 = n-Propyl alcohol  
 Curve 5 = sec-Butyl alcohol  
 Curve 6 = n-Amyl alcohol

So in capryl alcohol the rubber has already an ideal volume of about 4 times its own weight.

But at 60°, the whole amount of added capryl alcohol is taken up by the rubber, and one could compare this system with the system rubber-benzene. On lowering the temperature a separation suddenly occurs. Apparently the ideal volume decreases here with the temperature, and one gets a separation of the rubber with its solvate liquid. This can be repeated as often as required.

The experimental data show that if a system made at 60° is cooled, a separation occurs suddenly at a temperature dependent on the concentration, but lying between 41° and 43° for not too dilute systems. If one leaves such a system for some weeks in the thermostat at 40°, one gets two perfectly clear layers. Further cooling gives then only a very slight cloudiness of the under layer. This indicates that below 40° the ideal volume remains practically constant. So at about 43° there is

a very rapid change of this ideal volume, a change from 4 times the particle weight to a much higher value.

Pummerer<sup>13</sup> was the first who observed this phenomenon; yet he did not see it was a separation. He simply described it as apparently a question of insolubility.

If, however, one tries to analyze these layers, the concentration of the upper layer is found to be dependent on the concentration of the rubber in the original solution before the separation. Hence we are dealing not with a simple binary system but with a system of more than two components.

Our discussion of the facts of Fig. 5 needs no alteration from this observation of the heterogeneous character of rubber. For in these cases all the rubber acts as if it were a homogeneous system and in the upper layer there is only, or practically only, the pure medium.

So with capryl alcohol at about 43° the amount of solvate increases suddenly to such values that all the rubber apparently dissolves in the medium. This case is a link between the cases of rubber-carbon tetrachloride and rubber-acetone. We expected now that it might be possible to show that, by changing temperature, the type rubber-carbon tetrachloride changes to the type rubber-acetone. Therefore sols of rubber in benzene, carbon tetrachloride, chloroform, toluene, and ether were cooled to their freezing points. But only in the case of rubber-ether was an effect observed. This effect is already quoted by Pummerer and Andriessen.<sup>14</sup> A sol in ether shows a somewhat unusual behavior; hence it is doubtful if one can draw conclusions from this fact to support our theory.

We could also try to see if for instance the system rubber-acetone can be altered to the type rubber-benzene by increasing the temperature. Unfortunately the boiling point and the decomposition are then factors which do not permit one to go to a very high temperature. Therefore no attempts in this direction had any result.

My thanks are due to Professor F. G. Donnan, for his vivid interest taken in this work.

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# Studies on the Nature of the Action of Organic Accelerators of Vulcanization

## The Action of Organic Accelerators on Rubber Sols I-III

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While there is a difference of opinion as to the exact mechanism involved, it is generally agreed that the action of organic accelerators in hastening the vulcanization process is usually attributed to the conversion of the sulfur into an active form, probably through the intermediate formation of a compound capable of yielding "nascent" sulfur.

But some workers, (Ames, *J. Soc. Chem. Ind.*, **43**, 117T (1924); Kirchhof, *Kolloid-Z.*, **14**, 35 (1914); Twiss, *J. Soc. Chem. Ind.*, **35**, 782 (1917); Ditmar, *Z. angew. Chem.*, **34**, 465 (1921)) have suggested that the action of organic accelerators might be on the rubber hydrocarbon itself. This theory has not been generally developed, though it has received some small amount of evidence through the works of Le Blanc and Kröger (*Z. Elektrochem.*, **27**, 335 (1921)) and Naunton (*J. Soc. Chem. Ind.*, **44**, 243T (1925)). These investigators found that the viscosity of rubber solutions decreased with the introduction of an organic accelerator, and referred this phenomenon as a "depolymerization" of rubber. These observations possibly suggest that the influence of accelerators is exerted upon the rubber and constitute the only direct evidence in favor of this view.

Nevertheless, an examination of the chemical composition of various accelerators warrants the assumption that they do not all function in the same manner, since they differ so widely in their structures and basic properties, so that it seems very doubtful that all accelerators cause a reduction in the viscosity of rubber solutions in a similar manner. Moreover the term "depolymerization" is not strictly accurate, because it is not yet confirmed whether the change which is characterized by the diminution of the solution viscosity is a chemical one involving a reduction in the size of the rubber molecules or of a physical nature due to a reduction in the state of aggregation. The present author is aware of the fact that if an accelerator is capable of causing depolymerization of the rubber, it must play an important role in the vulcanization process; yet scarcely any effort has been made to explain the exact nature of organic accelerators. From this viewpoint, the author has studied the action of organic accelerators on rubber sols by following the change of the solution viscosity, in order to ascertain what types of accelerators can really give rise to the depolymerization of rubber molecules. In the following communication he hopes to be able to point out some interesting and characteristic properties of organic accelerators hitherto quite unknown.

About one gram of first latex crepe was dissolved in 100 cc. of purified benzene after a 12-hour extraction with acetone. After the small quantity of impurities had settled, the liquid was filtered through glass wool, the solution thus obtained being entirely clear. This benzene sol was diluted to a concentration of 0.4% (g./cc.), and was kept in the dark until used. The viscosity measurements were made at

constant temperature ( $23 \pm 0.02^\circ \text{C.}$ ) using an Ostwald viscosimeter constructed with brown colored glass with a capillary diameter of 0.5 mm. Ten cc. of the benzene sol were introduced in the viscosimeter, and to this 0.004 gram of an accelerator previously dissolved in one cc. of benzene was added by means of a 1-cc. pipette. In order to prevent local desolvation, which would be produced at the point of entry of the accelerator, the mixed solution was agitated for a little while by introducing a stream of dry nitrogen in the viscosimeter. After 15 minutes was allowed to elapse to assure complete dispersion of the accelerator in the sol, the viscosity measurements were carried out at intervals of 10 minutes during the early stages and later at longer intervals. Since the measurements were only relative, the time of

TABLE I  
INFLUENCE OF ZINC METHYLPHENYLDITHIOCARBAMATE ON THE VISCOSITY OF A BENZENE SOL

Time Elapsed in Minutes	Time of Flow of Solution in Seconds	Time Elapsed in Minutes	Time of Flow of Solution in Seconds
0	149.2	120	148.3
15	148.9	135	148.3
25	148.8	150	148.3
35	148.8	165	148.3
45	148.6	180	148.2
55	148.6	195	148.2
65	148.5	210	148.2
75	148.4	240	148.2
85	148.4	270	148.1
95	148.4	300	148.1
105	148.3		

TABLE II  
INFLUENCE OF HEXAMETHYLENETETRAMINE ON THE VISCOSITY OF A BENZENE SOL

Time Elapsed in Minutes	Time of Flow of Solution in Seconds	Time Elapsed in Minutes	Time of Flow of Solution in Seconds
0	156.0	105	151.4
15	152.1	120	151.4
25	151.8	135	151.4
35	151.7	165	151.4
45	151.7	180	151.4
55	151.7	210	151.4
65	151.6	240	151.3
85	151.6	270	151.3
95	151.5	300	151.3

TABLE III  
INFLUENCE OF DIPHENYLGUANIDINE ON THE VISCOSITY OF A BENZENE SOL

Time Elapsed in Minutes	Time of Flow of Solution in Seconds	Time Elapsed in Minutes	Time of Flow of Solution in Seconds
0	156.4	120	146.0
15	147.4	135	146.0
25	147.1	150	146.0
35	146.8	165	145.9
45	146.6	180	145.9
55	146.4	195	145.9
65	146.3	210	145.8
75	146.1	240	145.7
85	146.0	270	145.7
95	146.0	300	145.6
105	146.0		



TABLE IV

## INFLUENCE OF MERCAPTOBENZOTHAZOLE ON THE VISCOSITY OF A BENZENE SOL

Time Elapsed in Minutes	Time of Flow of Solution in Seconds	Time Elapsed in Minutes	Time of Flow of Solution in Seconds
0	156.4	120	137.6
15	153.1	135	135.3
25	151.6	150	132.7
35	150.1	165	131.1
45	148.6	180	128.1
55	147.4	195	125.6
65	145.8	210	124.1
75	144.3	240	117.5
85	143.0	270	113.0
95	141.6	300	107.8
105	140.1		

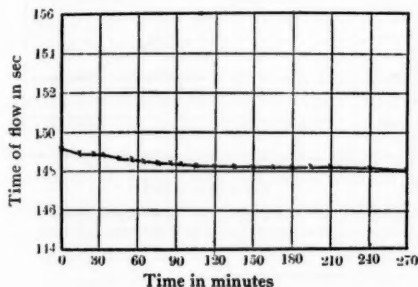


Figure 1—Influence of Zinc Methylphenyl Dithiocarbamate on the Viscosity of a Benzene Rubber Sol

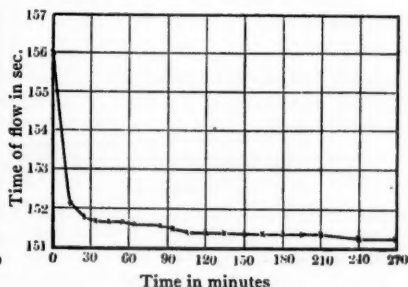


Figure 2—Influence of Hexamethylenetetramine on the Viscosity of a Benzene Rubber Sol

TABLE V

## INFLUENCE OF TETRAMETHYLTHIURAM MONOSULFIDE ON THE VISCOSITY OF A BENZENE SOL

Time Elapsed in Minutes	Time of Flow in Seconds	Time Elapsed in Minutes	Time of Flow in Seconds
0	156.0	120	140.8
15	152.8	135	140.0
25	151.6	150	137.9
35	150.2	165	136.1
45	149.0	180	134.5
55	148.2	195	133.0
65	146.5	210	131.6
75	145.8	240	128.4
85	144.8	270	127.0
95	143.5	300	126.1
105	142.0		

flow was measured in seconds. (Time of flow at  $t = 0$  shows the viscosity for a solution of 10 cc. of the sol + 1 cc. of benzene without accelerator.)

The samples of organic accelerators examined were thirty in all, but only a few of the experimental results obtained are given in Tables I-V.

It has been found from an examination of the results that the organic accelerators could be classified in three main groups, as shown in the following list, according to the manner in which they affect the rubber solution viscosity.

### Classification List of Organic Accelerators

The first group: anhydroformaldehyde-aniline, anhydroformaldehyde-*p*-toluidine, *p*-nitrosodimethylaniline, zinc ethylphenyl dithiocarbamate, zinc methylphenyl dithiocarbamate, zinc butylxanthate, lead dithiobenzoate, tetramethylthiuram disulfide, tetramethylthiuram tetrasulfide.

The second group: hexamethylenetetramine, ethylidene-aniline, acetaldehyde-aniline, heptaldehyde-aniline, triethyltrimethylenetriamine, diphenylguanidine, di-*o*-tolylguanidine, phenyl-*o*-tolylguanidine, triphenylguanidine, *o*-tolylbiguanide, piperidinepentamethylene dithiocarbamate, cyclohexylamine dithiocarbamate.

The third group: thiocarbanilide, di-*o*-tolylthiourea, *p*-nitrosophenol, nitroso-

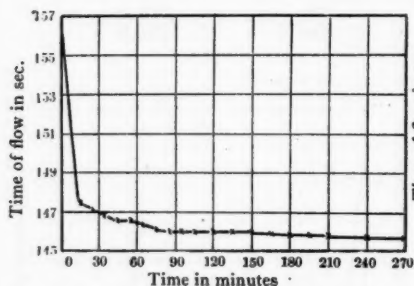


Figure 3—Influence of Diphenylguanidine on the Viscosity of a Benzene Rubber Sol

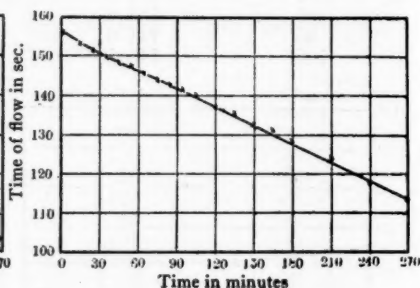


Figure 4—Influence of Mercaptobenzothiazole on the Viscosity of a Benzene Rubber Sol

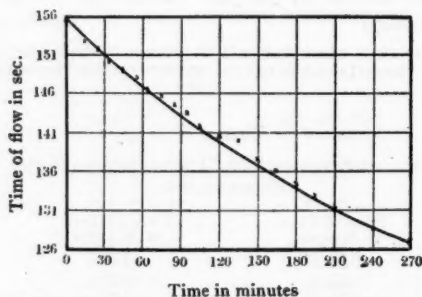


Figure 5—Influence of Tetramethylthiuram Monosulfide on the Viscosity of a Benzene Sol

benzene, mercaptobenzothiazole, dibenzothiazole disulfide, thioetophenyldi-propylpropylenedihydrothiazine, tetramethylthiuram monosulfide, dinitrophenyl-ester of dimethyldithiocarbamic acid.

The accelerators belonging to the first group have almost no influence on the viscosity of rubber sols, while those of the second and third groups reduce the viscosity of the solution to a marked degree, but the manner in which they affect the viscosity differs utterly. The second group produces its effect on the viscosity practically at once, as shown by the time curves for hexamethylenetetramine and diphenylguanidine given in Fig. 2 and Fig. 3, whereas the effect on the viscosity, of the third group is not thus immediate, but, instead of coming sharply to an end continues over a long period of time, as the progressive fall in viscosity produced by mercaptobenzothiazole or tetramethylthiuram monosulfide (shown in Fig. 4 and Fig. 5) demonstrates.

It has been suggested by Naunton (*loc. cit.*) that a comparison of the effect upon the viscosity of a rubber solution of organic accelerators could be utilized as a means of testing the action of accelerators, but the author believes such a method does not give reliable results, since great anomalies are met on comparing the organic accelerators, as shown in the above list. It is not, therefore, of general application.

Considering the different manner in which the accelerators of the second and third groups affect the viscosity of rubber sols, it would appear to be necessary to distinguish between the action of the accelerators of the two groups. The author (*J. Rubber Soc. Japan*, 3, 413 (1931)) has previously studied the action of heat on xylene-rubber sols and presumed that the change which rubber solutions undergo on heating would be depolymerization, *i. e.*, the change would be rather a chemical one involving a breaking up of the rubber molecules. The time curve representing the effect of heating was almost identical with those representing the influence of the third group accelerators. From this fact, the author presumes that the characteristic action of the third group members is to be regarded as due to depolymerization of rubber molecules.

The second group accelerators, on the other hand, do not affect the viscosity in the same manner, so it is unlikely that their effect is explicable by depolymerization. Accordingly the author proposes a new hypothesis that the action of the second group accelerators is rather of a physical nature involving disaggregation, *i. e.*, their general effect is to cause a reduction in the state of aggregation. It is a quite noteworthy feature that these accelerators are amines or amine derivatives, all of which have without exception basic properties. Up to the present time, countless attempts have been made to distinguish between the "depolymerization" and "disaggregation" of rubber molecules, where in many cases the difference is merely one of definition. The author has indicated that some accelerators would probably be capable of causing chemical depolymerization and others of causing physical disaggregation. This theory, which would be quite suggestive for a study of the colloidal nature of rubber, may be considered as a contribution to the difficult problem of rubber vulcanization.

In this paper the author has considered the effect of organic accelerators on rubber sols, but the information given is more of a hypothetical or qualitative nature, and should be reduced if possible to a quantitative basis. More definite explanations for the experimental results obtained will be reported in a later publication.

# Experiments on Oil-Proof Rubber

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## I. PRELIMINARY REPORT

### Introduction

There is a great demand for electric wires with a superior oil-resistant insulation for use in ships, airplanes, and automobiles. The wiring of generators, transformers, and other electric vehicles is also damaged by oil. Other cases of the direct or indirect injury of rubber products by oil, are rubber hose, rubber pails, etc., which are used in oil-refining and transportation, and rubber rollers in printing and dyeing. These rubber products swell up, lose mechanical strength, and become useless.

Oil-proof rubber has been studied considerably and various patents have appeared. In some cases the protection is obtained by compounding with inorganic substances, soap or glue. Another method is to overvulcanize until the product is a semihard rubber, and still another is to apply an oil-resistant coating on the rubber.

The object of the experiments which are described is to find a superior method of oil-proofing rubber so that it can be vulcanized under the best conditions and be soft and elastic.

Special studies were made of compounds to find whether the best ingredients are organic or inorganic, light or dense, fine or coarse, etc., and also to find whether or not these differences cause any change in the chemical structure of the rubber.

### Preparation of Samples

The base compound was:

	By Weight	By Volume
Washed pale crepe	98.0	106.3
Acid-free sulfur	3.0	2.0
Diphenylguanidine	0.8	0.8
Zinc oxide	5.0	0.9
Total	106.8	110.0

To this base compound, 20 parts by volume of the following ingredients were added, as indicated in Table I. These were made into sheets of 4 mm. thickness and vulcanized at 45-lb. steam pressure per square inch.

The optimum time of vulcanization for the base compound, as judged by mechanical tests, was about 40 minutes. Since it was laborious to find the optimum time of vulcanization of each of the above compounds, the times of vulcanization were limited to 30 and 60 minutes for each compound. The vulcanized samples were tested at a certain time after vulcanization for mechanical strength.

### Experimental Procedure

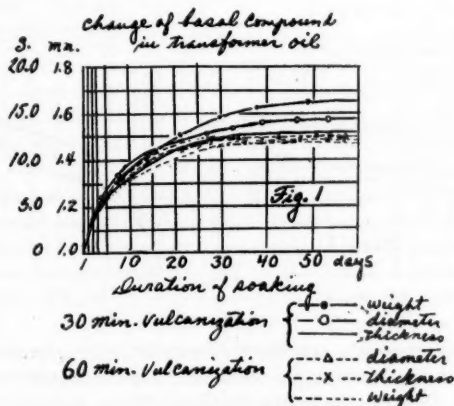
After recording the weight, diameter, and thickness, all samples for the oil-absorption test were placed in oil to be tested. The oils used at first were gasoline, transformer oil, and lubricating oil, but gasoline was unsatisfactory. The transformer oil, supplied by the Standard Oil Co. of New York, had a clear, reddish

brown color, with  $d^{15}$  0.882, viscosity at 30°, 2.65; the lubricating oil,  $d^{15}$  0.874, viscosity at 30°, 8.34. The samples immersed in oil were taken out at certain intervals of time, drained, and wiped. The changes in weight, diameter, and thickness were determined, and the samples were then returned to the oil. The samples were immersed in oil for 1, 2, 3, 5, 10, 20, 30, and 60 days, respectively, at room temperature.

TABLE I  
INGREDIENTS USED IN COMPOUNDING

Sample No.	Ingredient	Per Cent by Wt.	Sample No.	Ingredient	Per Cent by Wt.
1	Talc powder	54	17	Zinc sulfide	80
2	Kaolin	54	18	Titanium white	76
3	"Catalpo" clay	50	19	"Hakuenkwa" cc. <sup>a</sup>	54
4	"Aluminum flake"	52	20	"Crimson antimony"	68
5	Zinc oxide	112	21	"Vandex" (selenium)	96
6	Magnesium oxide	70	22	Cement	56
7	Magnesium carbonate	46	23	Reclaimed rubber	20
8	Calcium oxide	48	24	Glue	20
9	Calcium carbonate	54	25	Soap	20
10	Litharge	180	26	Starch	20
11	Lithopone	86	27	Paraffin	20
12	Barytes	84	28	Powdered ebonite	20
13	Kieselguhr	36	29	Black salve	20
14	Iron oxide	96	30	Gutta-percha	20
15	"Cosmos" carbon	36	31	Coumarone resin	20
16	"Thermatomic" carbon	36			

<sup>a</sup> A commercial preparation containing zinc oxide.



The absorption of oil was measured in two ways. One was to measure the increase in diameter and thickness of the samples, the other to find their increase in weight. There were some errors in measuring the increase in diameter because of irregularities of shape, and though the errors in measuring the increase of thickness were not so large as with the diameters, the measurements were difficult when the samples became soft from the absorption of oil. The errors in the gravimetric method were due to the solubility of rubber in oil and the volatilization of the oil, but these errors were almost negligible except with gasoline, which was partly lost by volatilization. The samples were weighed to the second decimal point, which was sufficiently accurate for comparison.

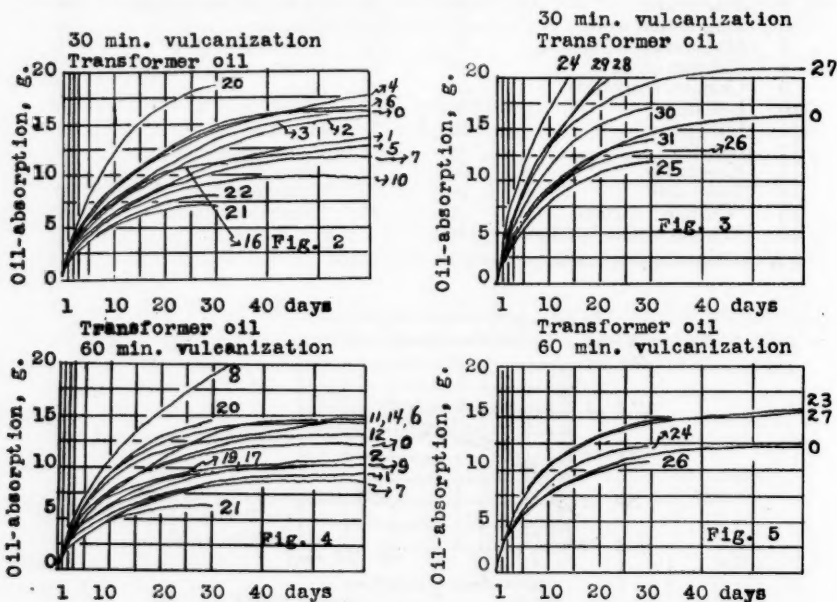


The results on the base compound are shown in Fig. 1. The changes in diameter and thickness are shown in the figure for further comparison, since only the change in weight was considered as absorption of oil.

### Results

The results show no marked difference during the first ten days in oil absorption between the samples vulcanized for 30 and 60 minutes, but the sample vulcanized 60 minutes showed less absorption after that time. The rate of absorption was greatest during the first few days (3-5 days in lubricating oil and 5-7 days in transformer oil), after which it decreased.

The results obtained on samples compounded with various ingredients are shown in Figs. 2-5 (transformer oil) and Figs. 6-7 (lubricating oil). The tendency of these to absorb oil was nearly the same as that of the base compound. There seemed



to be considerable differences in the speed of vulcanization, because of the different ingredients used in compounding, as some ingredients apparently caused an accelerating action in 30 minutes' vulcanization. Since the optimum time of vulcanization for samples Nos. 1 to 31 was not estimated, there must have been some irregularities in the degree of vulcanization which would tend to obscure the result.

The oil absorption indicated in the diagrams shows that there was considerable variation between rubber compounded from the base compound (curves indicated by 0 in figures) with the different ingredients.

Ingredients like carbon black, kieselguhr, lithopone, barytes, iron oxide, calcium carbonate, etc., are said to retard vulcanization, whereas magnesium carbonate, magnesium oxide, litharge, "Vandex," etc., accelerate it. The results with these ingredients were not clear.

Rubber compounded with "Vandex," litharge, calcium carbonate, cement, etc., showed a smaller oil absorption because of the formation of an extremely hard

rubber. It was not the object in this work to measure oil absorption on other than a soft and elastic product.

Compounds made with well vulcanized ebonite, which is of practical interest, resulted in a complete failure as was also the case when using reclaimed rubber. In this experiment the result of using glue was not satisfactory, since commercial glues are not uniform in quality. This will be discussed elsewhere. Paraffin and "black salve" were unsatisfactory, as they caused high oil absorption and swelling. A toilet soap gave a comparatively good result. The oil absorption of the sample compounded with starch was also low and the product showed no tendency to form hard rubber.

The hardness of rubber usually increased with 20 parts by volume of carbon black, but "Thermatomic" gave a comparatively soft rubber, as did barytes and lithopone, and showed much less oil absorption. It is suitable for oil-resistant rubber. Though the use of kieselsguhr and talc are said to retard the vulcanization, the compounds containing these substances showed an unexpectedly low oil absorption. The other ingredients which gave good results are kaolin, "Catalpo," zinc sulfide, titanium white, and "Hakuenkwa."

30 min. vulcanization  
Lubricating oil

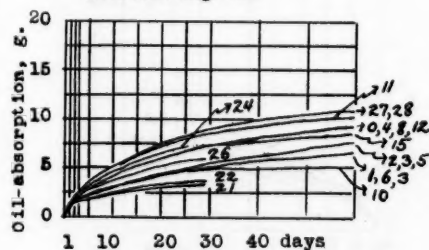


Figure 6

60 min. vulcanization  
Lubricating oil

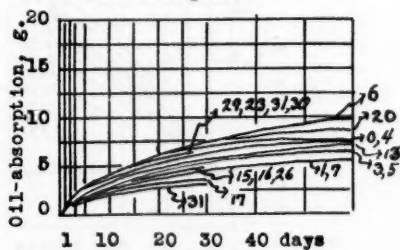


Figure 7

The question arising now is: "What is the substance in the sample which absorbs the oil?" Should the absorption of oil be caused only by the rubber-sulfur system, compounds with other ingredients should show proportionally less oil absorption. Suppose the absorption of oil by the base compound is 100 per cent, then the samples compounded with 20 per cent by volume of the ingredients should have 84.6 per cent, if the oil absorption is not influenced by these ingredients. Compounds which agreed experimentally with the above theory are magnesium carbonate, litharge, "Thermatomic" carbon, soap, "Vandex," titanium white, and "Hakuenkwa." In making comparisons of the oil absorption of these compounds with the base compound, the speed of vulcanization should be equal. In practice, however, these ingredients, like litharge, magnesium carbonate, "Vandex," etc., accelerate vulcanization, consequently the decrease in oil-absorption is probably attributable to this cause. In other cases, an increase in oil-absorption may be attributed to a retardation of vulcanization caused by the ingredients and to the solubility of oil in these ingredients. It is extremely difficult to explain the mechanism of oil-absorption, though this is the fundamental problem in finding an oil-resistant rubber.

Even when the rubber-matrix and ingredient are mixed thoroughly, there may be pore spaces which permit entrance of oil. The oil thus entering is absorbed by the rubber and the rubber swells. Increase in the mechanical strength of the

compounded rubber is due to an increase of the free surface energy between the rubber-matrix and the ingredient, since rubber having the greatest mechanical strength possesses the greatest free surface energy, *i. e.*, contact between the rubber-matrix and the ingredient is more intimate. Examples of low oil-absorption rubbers are those compounded with ingredients like "Hakuenkwa," calcium carbonate, and zinc sulfide, which tend to increase the mechanical strength of the rubber, while ingredients like barytes, lithopone, and "Aluminum Flakes" give a rubber with high oil absorption.

### Summary

Rubbers compounded and prepared under the same conditions were tested for their lubricating and transformer oil-absorptive capacity. Though the changes in diameter and thickness were measured, the changes in weight gave the best results for comparison.

Rubber containing ingredients which accelerate vulcanization or increase mechanical strength gave relatively little oil-absorption, while compounds with ingredients without these merits showed poor oil-resistance.

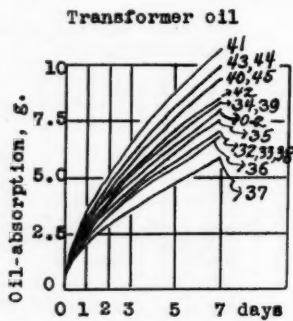


Figure 8

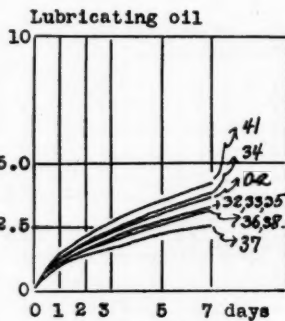


Figure 9

Rubber containing ingredients which are soluble in oil usually showed poor oil-proofing, whereas soap and starch gave good results.

### II. USE OF SOAP AS A COMPOUNDING INGREDIENT

The value of soap as a compounding ingredient is known already. The results with toilet soap were discussed in this preliminary report. Since ordinary alkali soaps are soft, and show no tendency to form hard rubber, they are of special interest because of their tendency to oil-proof the product.

An attempt was made to compare the results with a soluble alkali soap and with an insoluble metal soap.

#### Preparation of Samples and Experimental Procedure

All soaps used in this experiment were prepared in the laboratory, and for saponification stearic acid, linseed oil, and cocoanut oil were used.

The base compound contained pale crepe 98, acid-free sulfur 3, zinc oxide 5, diphenylguanidine 0.8. As there was no great difference in the density of the soaps, 2, 10, and 20 parts by weight of the soaps were added to the base compound. These were vulcanized at 45 lb. steam pressure per square inch for 30 and 60 minutes, respectively. Tests for oil absorption were made on the samples which gave the highest mechanical strength.

The size of the sample and the procedure were the same as in the preliminary experiment.

The oils used were lubricating oil, transformer oil and rapeseed oil, which were placed in a thermostat at  $30^{\circ} \pm 0.5^{\circ}$ .

As indicated in the preliminary experiment, the absorption of oil was greatest during the first 5-7 days, after which the rate of absorption was slow. Since it was found that the test after 7 days gave approximately correct results, determinations were made on the first, second, third, fifth, and seventh day.

### Results

The time of vulcanization and the mechanical strength of the samples are shown in Table II, and the oil absorption in Figs. 8 to 10.

*Results with 20 Parts of Soap.*—Though the rate curves of oil absorption were nearly linear in all cases, the amounts of oil absorbed varied greatly between the alkali soaps and insoluble metal soaps. Though the absorption of oil by the rubber

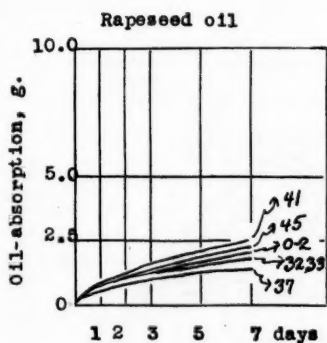


Figure 10

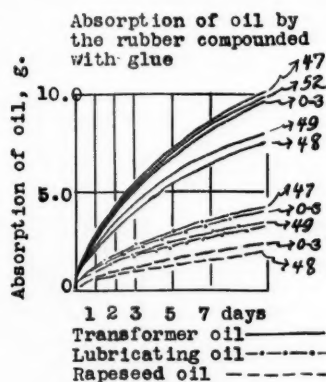


Figure 11

compounded with alkali soaps was very small and gave satisfactory results for oil-resistant purposes, metal soaps were unsatisfactory in all cases.

TABLE II  
MECHANICAL STRENGTH OF RUBBERS COMPOUNDED WITH SOAPS

Sample No.	Ingredient	Per-centage	Time of Vulcani- zation, Min.	Tensile Strength, Kg./Cm. <sup>2</sup>	Elonga- tion, %	Hardness (Shore)
0-2	Nothing	0	45	173.3	717	47
32	Sodium stearate	10	45	174.3	721	54
39	Potassium stearate	2	30	186.1	747	47
33	Potassium stearate	10	30	177.5	731	55
37	Potassium stearate	20	30	176.3	676	55
34	Sodium soap of linseed oil	10	30	178.5	792	50
35	Sodium soap of castor oil	10	45	125.3	705	53
36	Sodium soap of cocoanut oil	10	45	164.0	705	53
38	Sodium soap of cocoanut oil	20	30	158.3	738	50
40	Calcium stearate	20	45	144.7	786	48
41	Aluminum stearate	20	45	122.0	774	47
42	Magnesium stearate	20	45	148.2	807	51
43	Iron stearate	20	60	118.3	831	48
44	Zinc stearate	20	60	93.1	809	47
45	Zinc stearate	10	60	110.0	812	47

Among the alkali soaps, the absorption of oil was least in rubber containing potassium stearate. Sodium soap of cocoanut oil gave a rather high absorption in this group. Among the insoluble metal soaps, magnesium stearate gave the least oil absorption. It is noteworthy that the mechanical strength of the product from this soap was satisfactory. The mechanical strength of rubber compounded with "Aluminum flake" was not good, and the absorption of oil was highest, *i. e.*, nearly twice the absorption of the sample compounded with potassium stearate.

*Results with 10 Parts of Soap.*—In contrast to the control, potassium and sodium stearate and the sodium soap of cocoanut oil decreased the absorption, while the sodium soap of linseed oil gave a slightly increased oil-absorption. In contrast to 20 parts, the decrease in the amount of soap did not have a striking effect on the oil-absorption of the sodium soap of cocoanut oil, but the difference was very great with potassium stearate. Accordingly, a test was made with only 2 parts of potassium stearate. The mechanical strength was good in this product, but the absorption of oil was greater than in the control sample. The general indications were that, in transformer oil, rubber compounded with the sodium soap of cocoanut

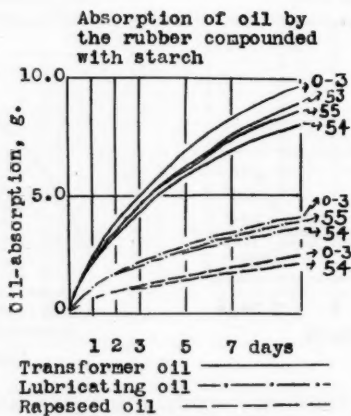


Figure 12

oil gave the most satisfactory result, potassium and sodium stearate less so, and alkali soaps of linseed oil and castor oil the poorest results. Lubricating oil and rapeseed oil were nearly identical to transformer oil, but the quantities of oil absorbed by the rubber were much smaller with rapeseed oil.

### Summary

The quantities of oil absorbed and the extent of the damage by oil absorption was greatest in transformer oil, less in lubricating oil, and least in rapeseed oil.

The absorption of oil was least with alkali soaps, while insoluble metal soaps gave a very high and unsatisfactory oil-absorption.

Alkali soaps made of stearic acid and cocoanut oil gave the best results.

### III. USE OF GLUE AS A COMPOUNDING INGREDIENT

Though it is known that glue or gelatin can be used as an ingredient in the compounding of oil-resistant rubber, and a few articles have recently dealt with this problem, the author was unable in a preliminary experiment to find any advantage



in glue. As commercial glue and gelatin vary greatly in quality, an attempt was made to compare these products.

It was found that thorough mixing of rubber and glue is difficult, especially when a large proportion of glue is used.

### Experimental Procedure

The glues used were an imported glue of good quality and three grades of home-made glue.

The samples were crushed and soaked for 24 hours with an equal quantity of water. The softened glue was added little by little to the rubber during milling. The moisture contained in the glue disappeared during the milling process and did not cause porous rubber when vulcanized.

The base compound contained rubber 98, acid-free sulfur 3, zinc oxide 5, diphenylguanidine 0.8, as in the previous experiment.

The compounds and the mechanical strengths of the products are indicated in Table III.

The tests for oil-absorption were carried out as in the previous experiment, *i. e.*,

Absorption of oil by the rubber compounded with different accelerators

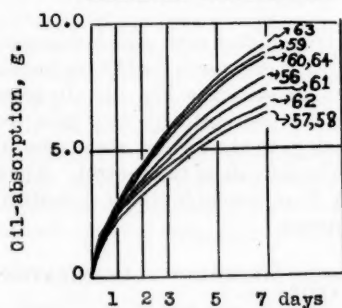


Figure 13

Relation between hardness and oil-absorption

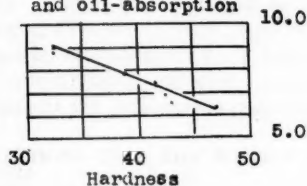


Figure 14

immersion of the samples in transformer oil, lubricating oil, and rapeseed oil for 10 days at 30° C. The result is shown in Fig. 11.

### Discussion of Results

Home-made grade A glue gave the best result, followed by B. The other two were little if any different from the control. The result was clearer when using transformer oil.

TABLE III

Sample No.		Percentage Ingredient	Vulcanisation Time, Min.	Tensile Strength, Kg. per Sq. Cm.	Percentage Elongation
0-3		0	30	207.0	792
46	Imported glue	8	30	164.3	752
47	Imported glue	25	30	109.4	681
48	Grade A	30	60	82.6	693
49	Grade B	30	60	29.8	654
50	Grade C	5	40	190.0	777
51	Grade C	10	40	186.0	755
52	Grade C	25	40	138.0	745

The oil absorption was smaller with more glue, but this difference was not clear when grade C was used.

In general the mechanical strength of the rubber decreased when glue was added, and the glue retarded vulcanization. Though the glue itself was insoluble in oil, glue was surprisingly ineffective in oil-proofing the rubber.

### Summary

The use of glue for rendering rubber oil-proof was unsatisfactory in most cases, and it retarded vulcanization.

A relatively soft rubber was obtained with a large quantity of glue, but the mechanical strength of the rubber was diminished.

### IV. USE OF STARCH AS A COMPOUNDING INGREDIENT

Samples were prepared by adding the following ingredients to the base compound.

TABLE IV

Sample No.	Ingredient	Percentage	Time of Vulcanization, Min.	Tensile Strength, Kg. per Sq. Cm.	Percentage Elongation
53	Corn starch	25	30	153	741
54	Flour	25	40	143	681
55	Potato starch	25	30	165	762

The mechanical strength of the rubber compounded with starch was good, and since the milling of starch into rubber was easy, more starch could have been added.

The results of the oil tests of the products are shown in Fig. 12. In general all of them gave satisfactory results. Samples compounded with flour gave the least oil-absorption, while those with potato starch gave the highest absorption, though the amount of oil absorbed was far less than in the case of the control. The results suggest the possibility of using rice or barley flour, insoluble starch or dextrin, agar-agar, mannan, sugars, etc., for the same purpose.

### V. USE OF THE BASE COMPOUND WITH DIFFERENT VULCANIZATION ACCELERATORS

#### Introduction

In the preceding experiment the author described the use of various ingredients in compounding oil-resistant rubber, but no ideal ingredient was found. Rubbers compounded with those ingredients which increased the mechanical strength of the product showed less oil-absorption. The benefit from using any of the other ingredients depended upon the prevention of softening of the rubber by the absorption of oil.

Though it may be impossible to make an absolutely oil-proof product by any choice of ingredients, the proper selection of materials may improve the product.

Some accelerators have a special hardening action, whereas others give a rather soft rubber. When the accelerator causes no special hardening, the time of vulcanization can be increased so as to yield a more oil-resistant rubber.

In the preceding experiments, only diphenylguanidine was used as accelerator. Since it hardens the rubber and also changes the color of the products, several other accelerators were tried.

#### Experimental Procedure

Nine accelerators were selected, as indicated in Table V. To the base compound: pale crepe 100, acid-free sulfur 3, zinc oxide 5, was added accelerator 0.6-2.0, de-

pending upon the activity of the accelerator. The mixtures were vulcanized at 20 or 40 lb. per sq. inch steam pressure.

TABLE V

Sample No.	Accelerator	Parts	Steam Pressure, Lbs.		Tensile Strength, Kg. per Sq. Cm.		Percentage Elongation	Hardness (Shore)
			Vulcanization, Min.					
56	Vulkacit Thiuram	0.6	20	15	253.0	820	38-40	
57	Vulkacit P	0.6	20	15	305.0	714	47	
58	Thionex	0.6	20	25	239.0	733	42-44	
59	Vulkacit M	1.0	40	30	174.0	895	32-33	
60	Vulkacit DM	1.0	40	25	173.4	883	32-33	
61	Vulkacit D	1.5	40	40	249.0	735	41-42	
62	DuPont 808	1.0	40	35	259.0	708	42-43	
63	Vulkacit A	2.0	40	50	178.0	873	32-33	
64	Vulkacit H	2.0	40	80	192.2	834	35	

#### Experimental Procedure and Discussion of the Results

Vulcanized samples were cut into discs 44.4 mm. in diameter and 4 mm. in thickness, and immersed in the oil (30° C.).

The results were clearest with transformer oil, as is indicated in Fig. 13. The mixtures with Vulkacit M, DM, A, and H gave a relatively high-oil absorption, and those with Vulkacit P, Thionex, and DuPont 808 a relatively low oil-absorption. Vulkacit H gave the highest oil-absorption in all three oils. Thionex showed the least absorption in transformer oil and rapeseed oil, while Vulkacit P showed the least oil-absorption in lubricating oil. However, the difference between these two was not very clear, and they appear to be the best for oil-resistant purposes. The mechanical properties of the products from these two accelerators are excellent, except for a rather great hardness. The hardness and oil-absorption of the products indicated that the oil-absorption was a function of the hardness. Where there is no requirement of a low hardness, a rubber mixture can be vulcanized to a relatively high oil resistance by the proper choice of the time of vulcanization.

#### Summary

Tests of rubber mixtures compounded with nine different accelerators indicated that those with relatively great hardness have relatively little absorption and those with less hardness have more. Rubber products which are not required to be particularly soft can be made with fairly good oil-resistant properties by the proper selection of accelerators and by vulcanizing to the optimum point.

# The Effect of Particle Size of Zinc Oxide on the Physical Properties of Rubber\*

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NEW JERSEY ZINC COMPANY, PALMERTON, PA.

## Abstract

The particle size of the pigment may be expressed in terms of several average diameters, depending on the method of measurement. In this work three of these averages were considered; namely,  $d_1$ , which is the arithmetical mean,  $d_s$ , which is the average diameter from which specific surface is calculated, and  $D$ , which is the average diameter from which the number of particles per gram is calculated.

A series of samples was prepared and these three average diameters were determined. These samples were then compounded with rubber and several physical properties measured.

As a result of these tests it is shown that, in general, the physical properties vary directly as the specific surface and the number of particles per gram. However, if the number of particles per gram is maintained constant and the specific surface is varied, it was found that the physical properties vary directly as the specific surface. No such relationship was found when the specific surface was maintained constant and number of particles per gram varied.

It is further pointed out that the only satisfactory means of measuring the  $d_s$  diameter, and therefore the specific surface, is by some microscopic method which determines the size-distribution curve for the pigment.

That the particle size of the pigment is of primary importance in determining the physical properties of a highly pigmented rubber compound has long been recognized. Due to the technical importance of a knowledge of particle size, several methods have been proposed for its determination. Unfortunately, however, not all of these methods are designed to measure the same average diameter, and some confusion exists from an occasional failure to define clearly the average diameter which has been measured. There are several average diameters all of which are functions of the uniformity of the pigment, and even in products that are reasonably uniform there are often significant variations among them. If all the particles in the sample are of the same size, these several averages will be equal, but if this is not true, the average diameter which measures for instance, specific surface, will be different from the one which measures the number of particles per gram.

A lengthy discussion of the several average diameters and their significance is not warranted here, as the subject has been very extensively covered by Perrot and Kinney<sup>2</sup> and later by Green.<sup>3</sup> For the purpose of this paper a brief résumé of the significance of three of these diameters will be given.

" $d_1$ ," is the arithmetic mean diameter and may be determined by any method of direct microscopic observation<sup>4</sup> or projection<sup>5</sup> or by the photomicrographic method.<sup>6</sup> The diameter of a large number of particles is measured and the average

$\frac{\sum nd}{\sum n}$  is calculated.

The " $d_s$ " diameter, which is the diameter from which specific surface is deter-

\* Paper presented at Denver, Colo., meeting of Rubber Division A. C. S., August, 1932.

mined and the specific surface, may be calculated from the data obtained by the above mentioned methods by use of the equations:  $d_s = \frac{\Sigma nd^3}{\Sigma nd^2}$  and  $S = \frac{6}{\rho d_s}$ , where  $S$  is specific surface in square meters per gram,  $\rho$  is the density of the pigment in grams per cubic centimeter, and  $d_s$  is in microns.

The " $D$ " diameter, which is the diameter from which the number of particles per gram is determined, and the number of particles per gram, may also be calculated from these data by use of the equations  $D = \sqrt{\frac{\Sigma nd^3}{\Sigma n}}$ , and  $N = \frac{1}{\rho D^3}$ , where  $\rho$  is the density of the pigment in grams per cubic centimeter and  $D$  is in centimeters.

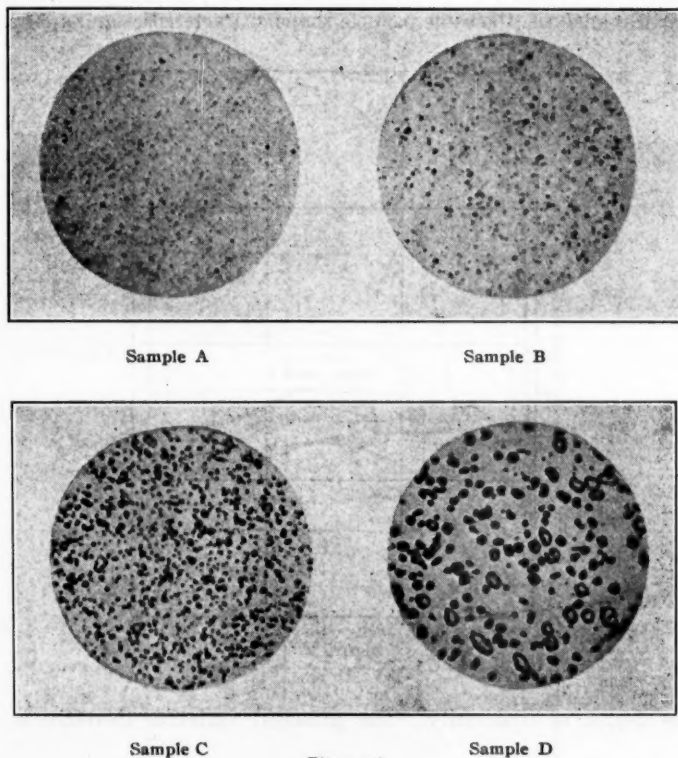


Figure 1

The count method proposed by Gehman and Morris<sup>1</sup> measures  $N$  and thus  $D$  directly and quite satisfactorily. No method of determining " $d_s$ " by measuring specific surface directly has been advanced that gives really satisfactory results. Methods involving the measurement of adhesion tension<sup>7</sup> and absorption<sup>8</sup> offer certain possibilities, but theoretical uncertainties have made these methods unreliable so far.

It is possible that the count method will give results that are a better measure of the absolute value of particle size than the photomicrographic method, but in order to carry out this investigation it was necessary to use a method which per-



mitted the determination of the several average diameters. It is felt that if the " $d_s$ " diameter as measured by the photomicrographic method is high, the " $D$ " is also high, so that the relation between these two diameters, as shown, is correct.

It is quite obvious that unless the physical properties of rubber which are considered functions of the particle size of the pigment follow the measured diameter, the method is of little significance. It is the purpose of this investigation, therefore, to establish which of the three above mentioned diameters,  $d_1$ ,  $d_s$ , or  $D$ , governs physical properties most closely and how great will be the error if an average diameter other than the correct one is used.

For this purpose we have selected four samples of zinc oxide, which will be shown as Sample A, B, C, and D. These materials for all practical purposes have the same chemical analysis, the same particle shape characteristics and approximately

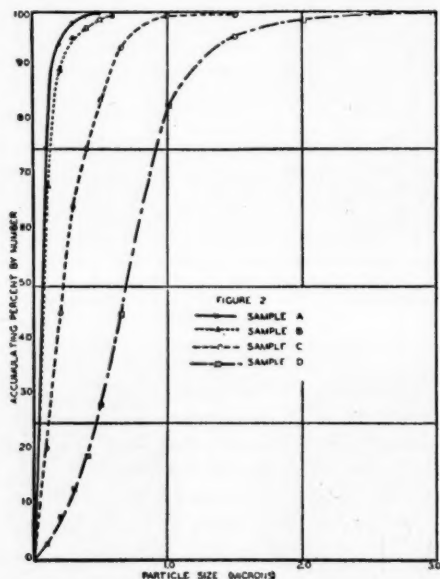


Figure 2

the same degree of uniformity. The principal variation therefore is particle size.

In Fig. 1 are shown the photomicrographs of the four samples of zinc oxide from which the particle size measurements were made. In the case of the finer oxides, A and B, ultra-violet light was used in the photomicroscopy in order to get the best possible resolution. This was not considered necessary in the case of the coarser oxides, as shown by the work of Haslam and Hall.<sup>9</sup> Three separate measurements were made on each sample, taking one photomicrograph of each of three samples of A and B and two of each of the three samples of C and D, so that in all cases at least one thousand particles were measured.

In Table I are shown the results of each of the three determinations as well as the average. The average size-distribution of the pigment particles is shown in Fig. 2.

TABLE I  
Sample A

	A	B	C	Average
$d_1$	0.134	0.132	0.130	0.132
$d_3$	0.228	0.202	0.200	0.210
D	0.173	0.162	0.160	0.165

Sample B

	A	B	C	Average
$d_1$	0.146	0.154	0.147	0.149
$d_3$	0.286	0.300	0.293	0.292
D	0.204	0.214	0.206	0.207

Sample C

	A	B	C	Average
$d_1$	0.337	0.345	0.349	0.343
$d_3$	0.684	0.725	0.711	0.707
D	0.490	0.519	0.507	0.502

Sample D

	A	B	C	Average
$d_1$	0.868	0.880	0.871	0.873
$d_3$	1.385	1.434	1.353	1.382
D	1.108	1.138	1.110	1.100

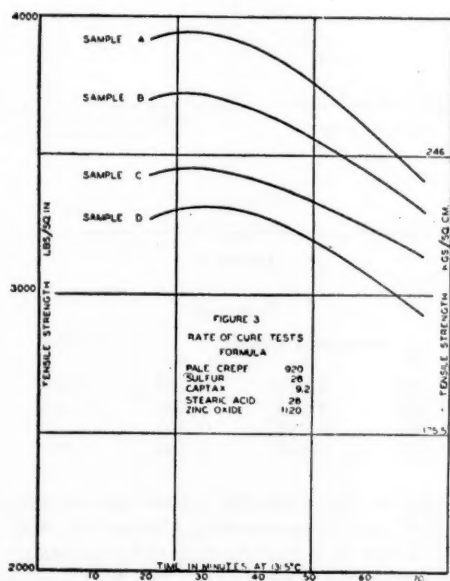


Figure 3

These four samples were then tested for a rate of cure in a mercaptobenzothiazole formula containing 20 volumes of pigment. The results are shown in Fig. 3. These curves show clearly that there are no differences in the curing characteristics of these four oxides. The cure of 25 minutes at 131° C. was used throughout. The differences in optimum tensile are, of course, a function of particle size, and show the range attainable with zinc oxides which vary only in that respect.

It was originally intended to consider three average diameters,  $d_1$ ,  $d_3$  and  $D$ , but calculations made to determine the variation in  $d_1$  for several mixtures of these four oxides showed that the value  $d_1$  was of no significance. For example, a mixture of 68 per cent of Sample A which has a  $d_1 = 0.132\mu$  and 32 per cent of Sample D which has a  $d_1 = 0.873\mu$ , had a  $d_1$  average diameter of  $0.133\mu$ .<sup>3</sup> The reason for this anomaly is that the arithmetical mean is so very markedly affected by the number of fine particles present that the addition of 30 per cent by weight of extremely large particle size material to a fine pigment does not appreciably change this value.

Subsequent testing of rubber compounded with various mixtures of these oxides showed that the change was much greater than that indicated by the change in this average, so attention was directed toward the other two averages  $d_3$  and  $D$ .

From the data in Table I it is possible to calculate the specific surface ( $S$ ) and number of particles per gram ( $N$ ). These values are shown below in Table II.

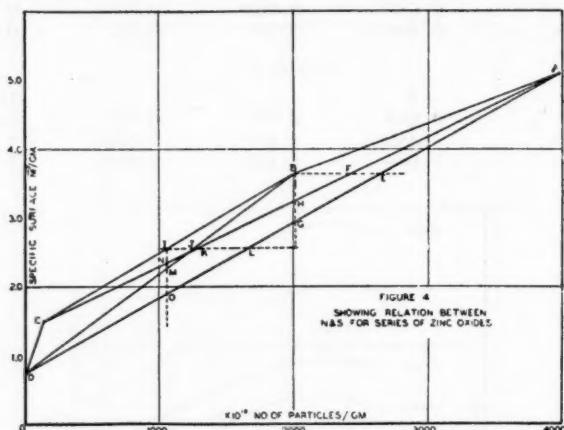


Figure 4

TABLE II

	Averages in Microns		$D$	$S$	$N$
	$d_1$	$d_3$		$M^{-2}/Gm.$	Number/Gm.
Sample A	0.132	0.210	0.165	5.08	$3975 \times 10^{10}$
Sample B	0.149	0.292	0.207	3.64	$2013 \times 10^{10}$
Sample C	0.343	0.707	0.502	1.51	$141 \times 10^{10}$
Sample D	0.873	1.382	1.100	0.77	$13 \times 10^{10}$

These data are plotted on Fig. 4, specific surface against number of particles per gram, the points A, B, C, and D representing the samples with those letters. By connecting the points A and B, a line showing the relationship between  $N$  and  $S$  for mixtures of these two oxides is obtained. The simple expedient of measuring the length of this line and calling it 100 per cent and measuring the distance from A to any point on that line will permit the determination of the percentage of each of the two pigments to be used in preparing a sample with any  $N/S$  ratio that is desired and which falls on the line. This can also be done between A and C, A and B, B and C, and C and D.

Starting with the point B, it was possible to get two samples: F, by mixing A and C; and E, by mixing A and D, which had the same specific surface as B but a varying number of particles per gram. By the same procedure, we obtained Samples H

and G, which had the same number of particles per gram but varying specific surface.

Repeating the procedure samples I, J, K, and L were prepared, all having the same specific surface but varying in the number of particles per gram; and I, N, M, and O of the same number of particles per gram but varying in the specific surface. The percentage of each of the original samples used in the mixtures prepared is shown in Table III.

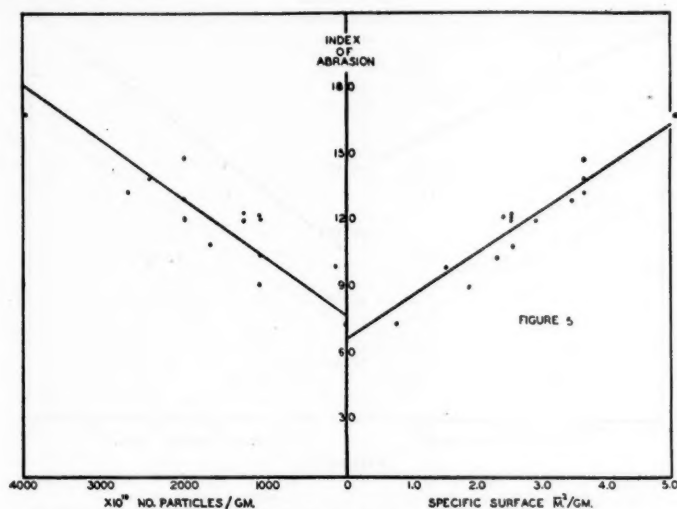


Figure 5

TABLE III

Sample	%A	%B	%C	%D
A	100	...	...	...
B	...	100	...	...
C	...	...	100	...
D	...	...	...	100
E	68	...	...	32
F	60	...	40	...
G	50.5	...	...	49.5
H	49	...	51	...
I	...	50	50	...
J	...	64	...	36
K	30	...	70	...
L	42	...	...	58
M	...	53	...	47
N	25	...	75	...
O	27	...	...	73

This series of samples was made by mixing the components through a flour sifter four times before incorporation into the rubber compound. A large master batch of all the ingredients in the formula except the zinc oxide was prepared to eliminate compounding variations. This formula was as follows:

Pale crepe	920
Sulfur	28
Mercaptobenzothiazole	9.2
Stearic acid	28
Zinc Oxide	1120

The pigment was incorporated with careful control of the temperature and time of milling to insure equal breakdown in all cases. The compounds were allowed to age 24 hours before curing and another 24 hours before testing. A number of physical properties were then determined and the results obtained are shown in Table IV.

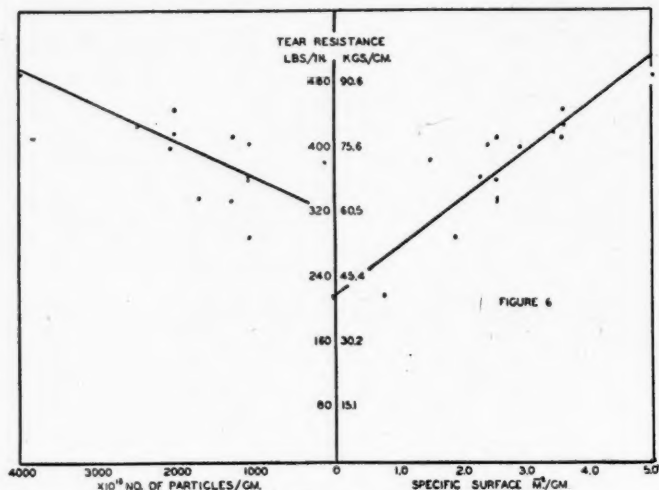


Figure 6

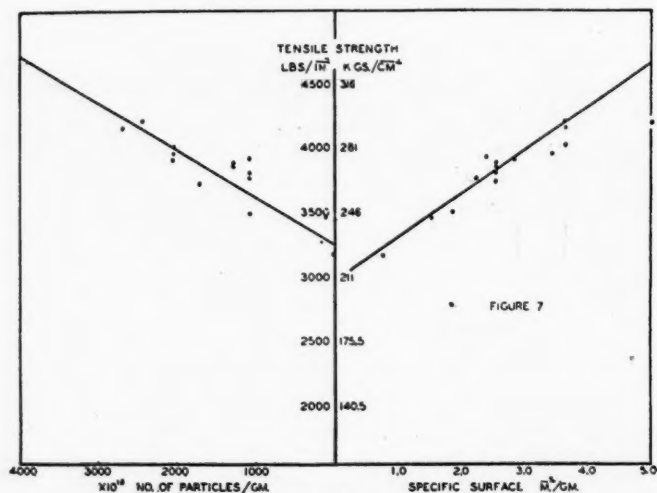


Figure 7

### Discussion

The data shown in Table IV have been analyzed and this analysis is here presented in two ways. The first and more general study has been to plot the specific surface and number of particles per gram for all the samples against several physical



properties which showed the maximum variation. From Fig. 5, the conclusion can be drawn that, in general, as specific surface increases abrasion resistance increases; and likewise, as number of particles per gram increases, the abrasion resistance increases. The relationship looks somewhat better in the case of specific surface.

Figure 6 shows the tear resistance, Fig. 7 the tensile strength, and Fig. 8 the modulus at 300 per cent elongation. The same general conclusions can again be applied.

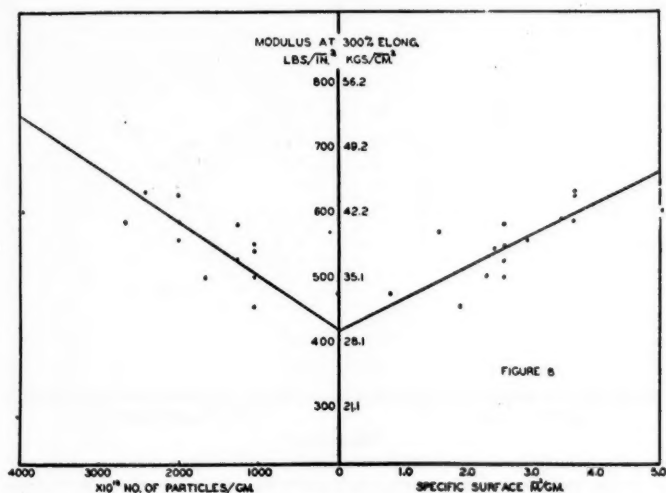


Figure 8

TABLE IV

	S	N	Abrasion Index <sup>a</sup>	Tear Resistance <sup>a</sup> Kgs./Cm.	Tensile Strength <sup>a</sup> Kgs./Cm. <sup>2</sup>	Modulus <sup>a</sup> 300% 450% Kgs./Cm. <sup>2</sup>	P. & J. Hardness	Energy of Resilience Kgs./Cm./Cc.	Plasticity 3' Plast. % Rec.		
	M <sup>-2</sup> /Gm. × 10 <sup>-10</sup>	× 10 <sup>-10</sup>	Index <sup>a</sup>	Kgs./Cm.	Kgs./Cm. <sup>2</sup>	Kgs./Cm. <sup>2</sup>					
A	5.08	3975	163	91	290	42	105	1.17	621	2.04	1.18
B	3.64	2013	144	82	280	43	104	1.13	605	2.03	0.74
C	1.51	141	95	70	240	40	100	1.09	440	1.95	0.41
D	0.77	13	70	39	218	33	79	1.14	418	1.84	0.38
B	3.64	2013	144	82	280	43	104	1.13	605	2.03	0.74
F	3.64	2440	135	79	292	44	105	1.08	565	2.05	0.88
E	3.64	2700	129	77	288	41	102	1.09	588	2.05	0.83
B	3.64	2013	144	82	280	43	104	1.13	605	2.03	0.74
H	3.44	2013	126	77	274	41	105	1.08	587	2.09	0.77
G	2.92	2013	116	74	271	38	98	1.07	568	2.01	0.90
I	2.56	1080	117	66	263	38	96	1.09	518	1.87	0.59
J	2.56	1260	115	61	269	36	87	1.15	524	2.03	0.59
K	2.56	1280	119	77	269	40	94	1.10	535	2.02	0.64
L	2.56	1700	105	62	260	35	81	1.11	507	1.98	0.76
I	2.56	1080	117	66	263	38	96	1.09	518	1.87	0.59
N	2.40	1080	118	74	274	37	91	1.10	526	1.98	0.81
M	2.28	1080	100	66	261	35	85	1.13	470	1.99	0.60
O	1.88	1080	87	53	242	31	82	1.11	456	1.93	0.62

<sup>a</sup> Average of two independent determinations.

A little closer scrutiny of the data, however, shows that further conclusions are warranted. In Fig. 9 are shown the abrasion data for those samples having the same number of particles per gram but varying specific surface. A rather marked trend is evident, *i. e.*, abrasion resistance increases as the specific surface increases.

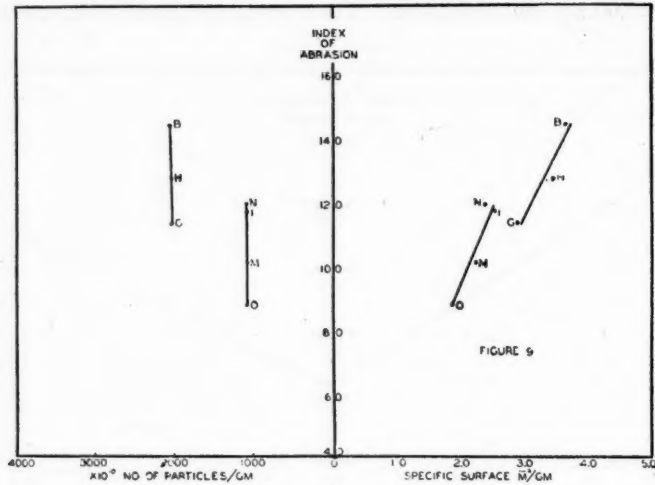


Figure 9

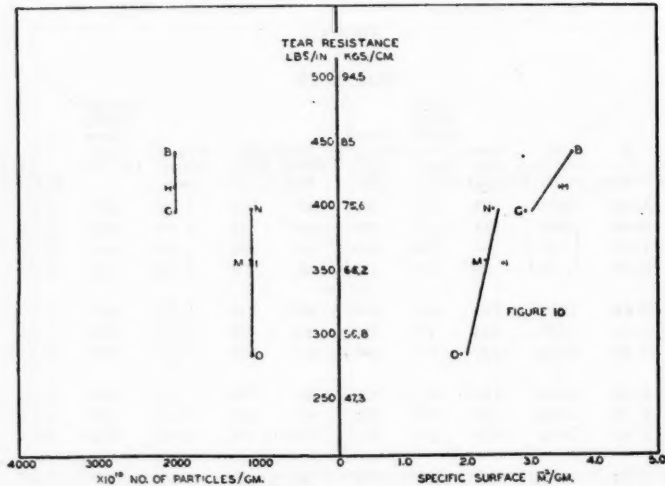


Figure 10

On analysis of the tear resistance data, Fig. 10 shows the same marked trend toward higher tear resistance with increased surface.

On the other hand an analysis of the series in which specific surface was kept constant and number of particles per gram was varied showed that no such definite trend was developed. Figure 11 shows the abrasion data, and Fig. 12 the tear data

for these samples. It is questionable whether any definite relationship exists here, but the indication is that tear resistance decreases with an increase in number of particles per gram, a conclusion that is not justified in view of the general conclusion drawn when all the data are considered.

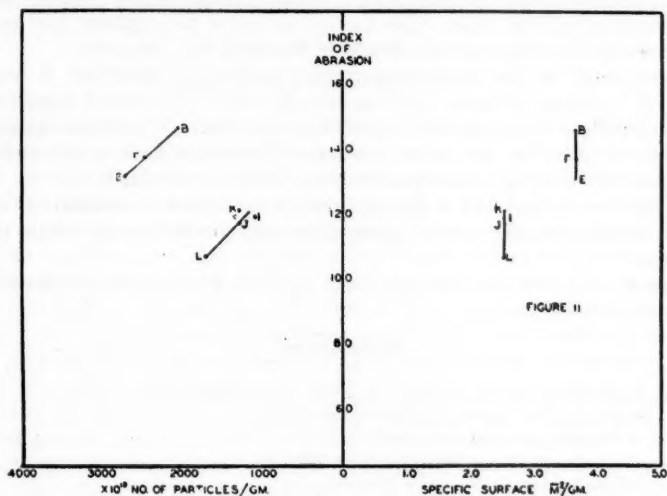


Figure 11

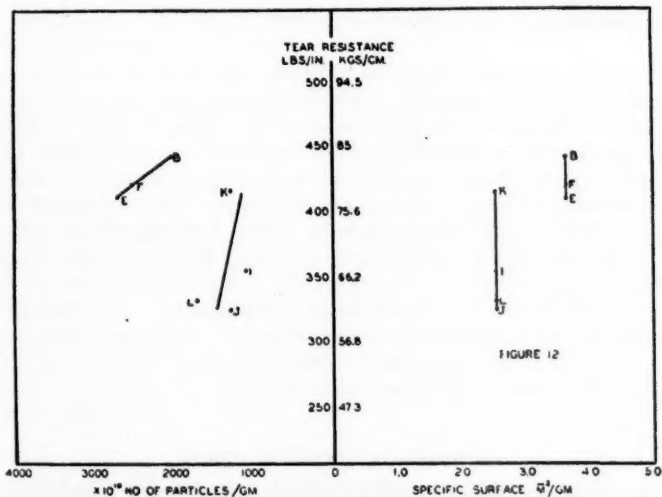


Figure 12

Considering Fig. 11, it will be noticed that while the specific surface is constant as evidenced by the vertical lines, the abrasion resistance varies somewhat. This variation is apparently a function of uniformity, for in one series Sample B is the most uniform; F, which is a mixture of A and C, is next; and E, which is a mixture of A and D, has the poorest uniformity. In the second series, I, which is a mixture

of B and C, is most uniform; J, K, and L follow in that order. This reasoning is further justified when applied to the other data.

### Summary

This paper offers further substantiation of the opinion that the reinforcement of a rubber compound is a function of the specific surface of the pigment, and any study of the mechanics of reinforcement should be based on this property.

When measured by the photomicrographic method as described, it was found that the " $d_s$ " average diameter and the specific surface calculated therefrom gave the best correlation with physical properties; that the " $D$ " average diameter and the number of particles per gram calculated therefrom gave a fair correlation, and that the " $d_i$ " average diameter gave essentially no correlation.

It was further shown that if the uniformity coefficient is maintained constant in a series of samples, any one of these diameters would have a certain practical significance.

The author acknowledges the assistance of C. H. Hall and N. A. Brown in the preparation of this paper.

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# Rubber Vibration Insulators

## Some Characteristic Properties and Tests

Franz D. Abbott\*

THE GOODYEAR TIRE & RUBBER CO., AKRON, OHIO

Insulating of vibrating parts of engineering devices and structures is one of the vital problems of this age. The original purpose of carriage and automobile tires was, as indeed the major purpose of their use today still is, the suppression and elimination of shocks and vibrations during travel. This is true in spite of the importance of the "increased mileage" obtained by the use of rubber tires—a factor of no mean importance. This purpose is not so self-evident in the case of belting, hose, rubber-covered rolls, etc., where flexibility and/or elasticity are apparently prime requisites, but nevertheless the interception and safe-transmission of impulses or stresses with a minimum of vibration and noise are certainly of inestimable value. The use of rubber parts elsewhere in the automobile and general engineering field is unquestionably solely for the suppression or elimination of vibration. Recognition of the importance of rubber parts for such service came with the organization early in 1927, at the request of the Society of Automotive Engineers, of a committee to make a study of the most important characteristics of rubber necessary in such service and finally to set up standards of tests for these properties. This committee was formed by the American Society for Testing Materials and is composed of a number of the leading automotive engineers of the country and rubber technologists from the leading rubber companies. The S. A. E. also has an official representative.

The scope of the work of this committee includes hardness testing, deflection under compression and compression-set (cold flow), resistance to cold, and dynamic fatigue, but to date its active efforts have been confined largely to the first two. The trend toward the use of rubber vibration insulators in railway work, both between ties and rails and in the cars themselves, is opening up a virgin field of enormous importance, and certainly shows the importance of these properties and the necessity for standardized tests. Of course, good aging qualities, resistance to abrasion, oil and heat, and relatively high tensile, shear, cutting and tearing strengths are important in the life of the part (but to varying degrees depending on the service intended). In addition, a standardized test for the adhesion of rubber to metal is now imperative. At present most specifications for motor supports in which rubber is bonded to metal require a direct pull, perpendicular to the metal-rubber interface, of 250 lbs. per sq. in. minimum, with actual values ranging up to over 1000 lbs. per sq. in.

### Design of Vibration Insulators

The actual sound and vibration deadening characteristics of rubber are functions not only of its resiliency, its "build-up" rate (since, in motor supports at least, this often determines a torque period), and allied properties, but also the interlocking factors of volume, dimensions (particularly those normal to the major applied stresses whether of compression, shear, or tension) and degree of stressing. Compounding and cure must be correctly established to ensure these properties, since

\* Chairman of Sub-Committee XVII A. S. T. M. D11 on "Rubber Products for Absorbing Vibration."



minor change in modulus may greatly influence the deflection rate of a stock. The rubber technologist specializing in the insulation of audible or material vibrations knows that a rubber part of a given quality, size, and shape will perfectly eliminate, for instance, the drumming of metal bodies or the sound transmission of all steel railway wheels, etc., yet may be either unsatisfactory for certain service (as a

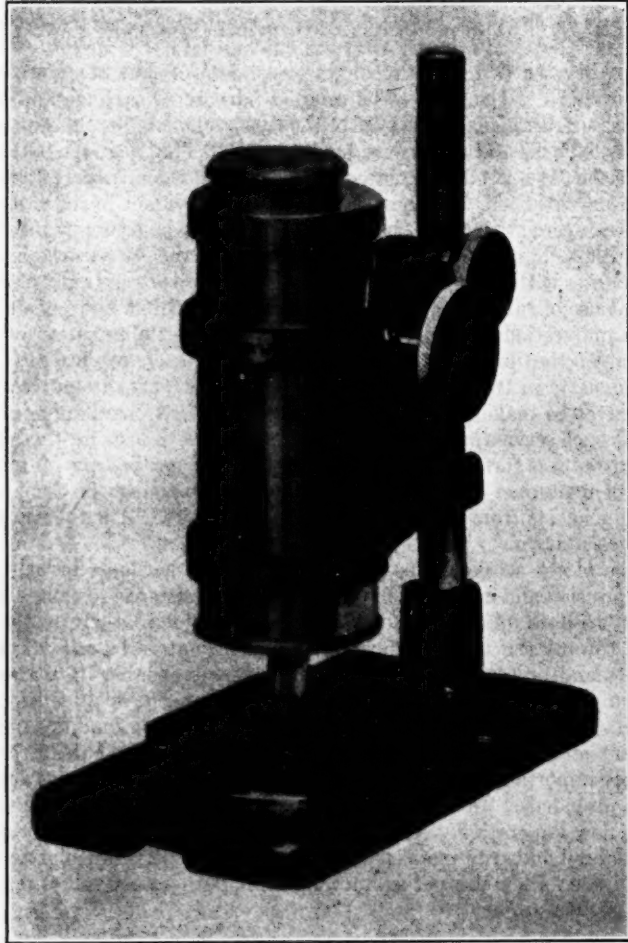


Figure 1—A. S. T. M. Rubber Hardness Tester (Tinlus Olsen)

Silent Bloc) or else of a quality far superior to that needed for some other service such as railway insulation pads between ties and the rails.

The sound deadening characteristics of a new part can be predicted to a high degree of accuracy for any given job and, conversely, the compound and dimensions of a satisfactory part can be predicted for a given job.

Consideration must be given also to the frequency and amplitude of vibration,

the unit static stresses, and the variations in these resulting from the vibrations and stressing, the effect of temperature on the stock, the deflection rate and compression-set of the stock, etc. Elimination of localized strains, friction, and fatigue failure is essential in the correctly designed insulator. The volume of rubber confined

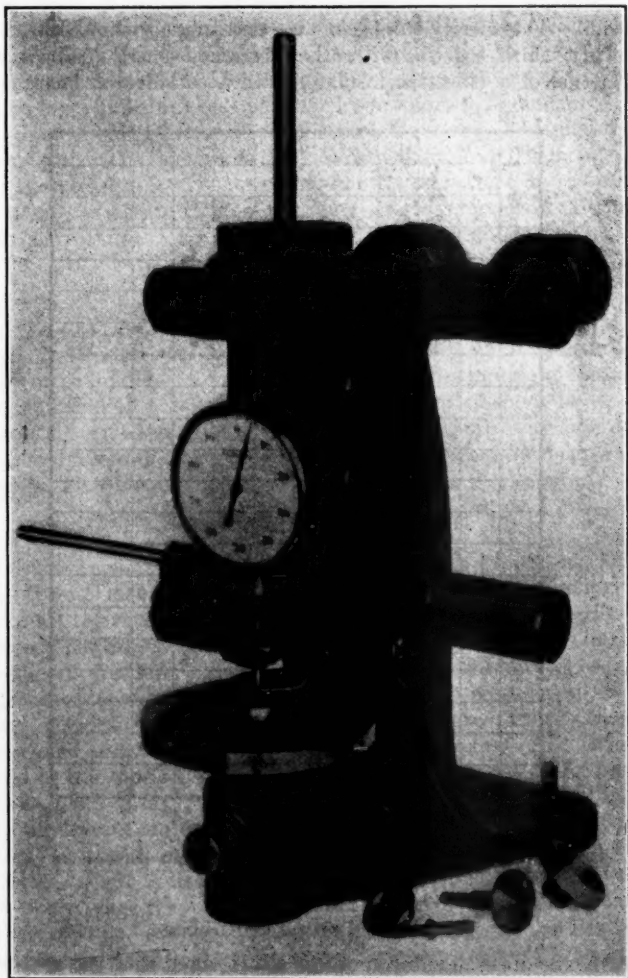


Figure 2—Rubber Hardness Tester (Hoopes and Lupke)

either under tension or compression should be sufficient to avoid localized stressing of a magnitude greater than the safe stress for that stock. Of course, if the service is extreme, a service assembly is the only perfect proof of the feasibility of an individual project, but often laboratory tests simulating actual conditions are very satisfactory, particularly if the stressing can be interpreted into service stressing or actual life.

The pioneer type of motor support in which the rubber was assembled under compression has largely been replaced in the last few years by the "V type" of support in which rubber bonded to metal is assembled under shearing (or tensile) stresses. However, compression assemblies of insulators will always far outrank other types. In fact the above-mentioned "V type" is now being supplanted by the novel "Floating Power" design in which the rubber is under compressive assembly loads. This merely emphasizes the necessity for standardized tests such as the following, which, together with other "common sense" qualities, will always ensure evaluation of a vibration insulator with a considerable margin of safety.

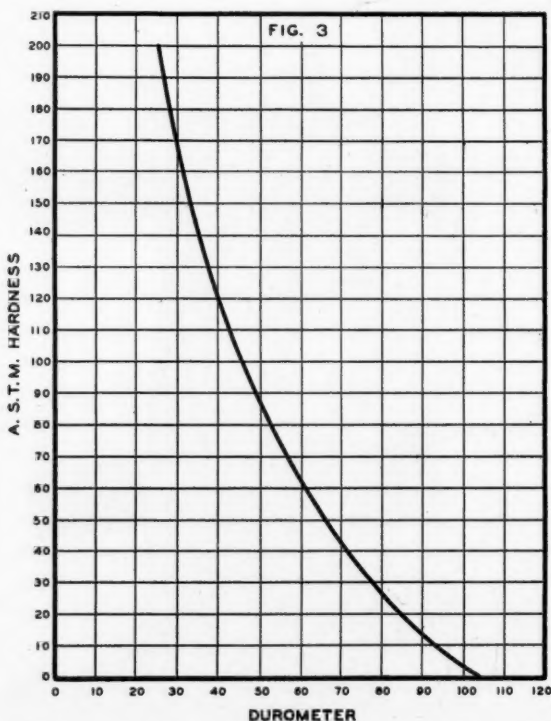


Figure 3—Relation between A. S. T. M. and Durometer Hardness Values

#### Hardness Testing of Rubber

The S. A. E. members of sub-committee XVII voted that the greatest need on vibration-absorbing rubber was for a satisfactory hardness tester "inasmuch as the existing dead-load instruments lacked flexibility, simplicity, and speed, whereas the commercial spring type instruments, though possessing these qualities, were reported as very unsatisfactory from a sensitivity and uniformity standpoint." The Committee reviewed the recommendations of all members as established by a questionnaire and has published<sup>1</sup> a tentative method of test for the hardness of rubber (D 314-31T). The method as published covers testing of the more common grades of rubber such as tire treads, most automotive mechanical parts, etc., but its intended scope is much larger. Admittedly, the actual hardness of

rubber (*i. e.*, its stiffness) is really its resistance to major body stresses such as those of bending or compression. However, these tests are not applicable to most vulcanized rubber parts (at least not in such a way as to establish comparative numerical data), whereas an indentation test is possible and, furthermore, it is indicative of the uniformity of the product. Consequently, for the purpose of this test, the hardness of vulcanized rubber is considered as that property by virtue of which the surface and adjoining layers resist indentation by an indentation element, the contact surface of which conforms to the surface of a portion of a true sphere  $\frac{3}{32}$  inches plus or minus 0.0005 inch in diameter, when subjected to a freely acting dead-weight load (pressure) of 3 pounds plus or minus 0.25 ounces. The indenter acts through an opening in the center of a pressure foot  $\frac{5}{8}$  inch plus or minus 0.005 inch in diameter. The opening is  $\frac{7}{64}$  inch plus or minus 0.005 inch. The contact surface of the pressure foot is parallel to the tested surface and is used as a zero reference point and also to "iron out" minor surface irregularities by lightly stressing the surface. A load of 5 pounds plus or minus  $\frac{3}{4}$  ounce acts on the pressure foot.

#### A. S. T. M. Hardness Number

The A. S. T. M. Hardness Number is the indentation, in thousandths of an inch, determined on samples of  $\frac{1}{2}$  inch gage and of 2 inches minimum lateral dimension and possessing smooth parallel faces, after application of the indenter and its load for 30 seconds. An average of at least five readings, taken at different places on the sample and differing by no more than 0.002 inch from the mean value, is taken as the standard hardness.

#### Hardness Testing Machines

Figure 1 shows a commercial A. S. T. M. Rubber Hardness Tester<sup>2</sup> developed by the Tinius Olsen Testing Machine Co., in conjunction with members of the committee, to meet their requirements. These requirements are primarily dead-weight load, accuracy not only in checking with different instruments but in tests with the same instrument over long periods of continued use, portability, speed of manipulation, and reasonable cost. The A. S. T. M. instrument possesses all the advantages of accuracy of a dead-weight instrument in which internal friction has been cut to a minimum, and also reliability over a long period of time. In these respects it is far superior to the spring type of instruments. It surpasses other dead-weight instruments in speed of operation, since reliable "comparative data" for check purposes or routine tests can be obtained as speedily as with the common spring type instruments. Figure 2 shows another instrument developed by Hoopes & Lupke to meet the A. S. T. M. specifications. Figure 3 compares A. S. T. M. hardness numbers with the average reading of a number of Durometers<sup>3</sup> on the same samples. Due to the variation between instruments of the spring type and to the introduction of error caused by the human element entering into tests by such an instrument, no absolute curve can be established. A comparison between A. S. T. M. and Pusey & Jones<sup>4</sup> data is given in curve I, Figure 4. Again, a curve of absolute values hard to establish in general use because of the human element entering into the tedious operation of dead-weight testers other than the A. S. T. M. instrument. Curve II, Figure 4, is a comparison of A. S. T. M. and Adams Densimeter hardness numbers.

Aside from the reliability (accuracy) and other points of acceptance of the A. S. T. M. instruments, their greatest importance is their use as a standard against which all other instruments can be standardized. Furthermore, A. S. T. M. hard-

ness data can be quoted or referred to in specifications as an absolutely definite set of data not depending on any particular instrument in a given laboratory.

The A. S. T. M. hardness testers are adaptable to extremely soft rubbers by the simple expedient of using a lighter load, or by the use of a needle point or "spear head" point for extremely hard rubber. Further work on these items is in progress. It is important to note, contrary to general opinion, that a very light test load is desirable for soft rubber, and that A. S. T. M. data obtained with a three-pound load are claimed to be a better criterion of the uniformity and service charac-

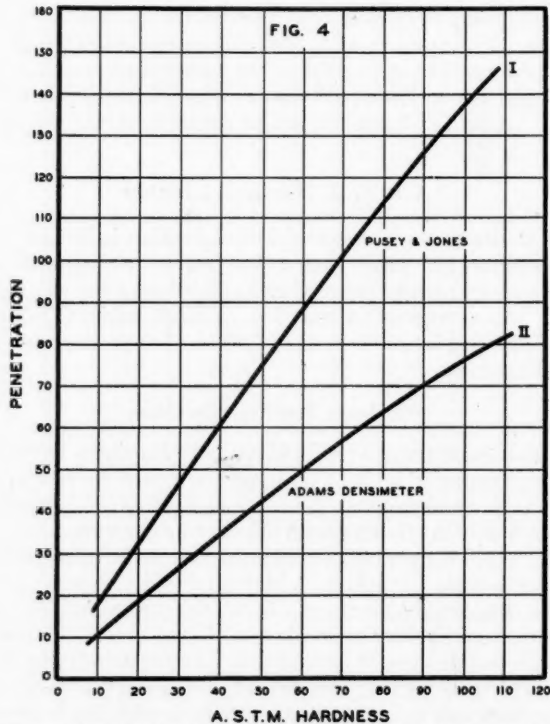


Figure 4—Relation between A. S. T. M. Hardness, Pusey & Jones and Adams Densimeter Penetration Values

teristics of a real soft motor-mounting (or similar stock) than any test, except possibly the compression-set test.

#### • Compression-Set (Cold Flow)

Resistance to permanent deformation under compressive stresses is perhaps the most important property of rubber used to absorb vibration because it is more indicative of the "service quality" of an insulator than any other single property, unless it be resistance to dynamic fatigue (flexure-set). The work of the "Cold Flow" section of sub-committee XVII is nearly completed. Some very important points of technique in making this test have become established<sup>5</sup> as of vital importance in performing this test. In fact, these latter test conditions are finding con-

siderable use for stocks of 30 A. S. T. M. hardness (80 Durometer) with a maximum of 10% compression-set allowed.

The extent to which distortion, expressed as a percentage of the original thick-

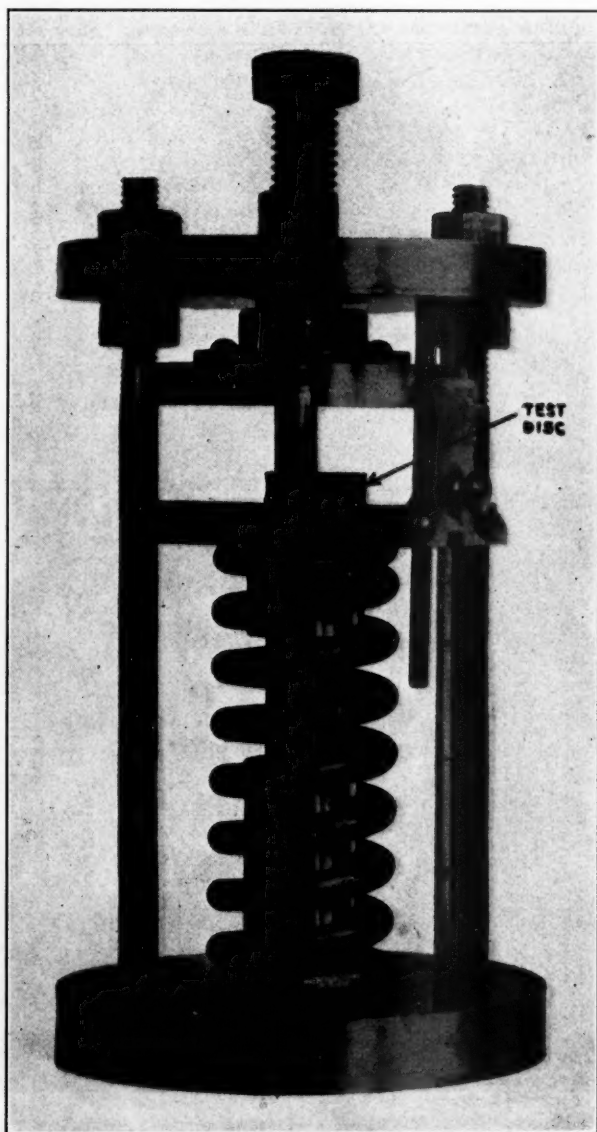


Figure 5—Compression-Set (Cold Flow) Testing Machine

ness, has become permanent after subjecting a test piece  $\frac{3}{4}$  inch in diameter and  $\frac{1}{4}$  inch thick to a load of 600 lbs. per sq. in. for 24 hours at 158° F. (70° C.) in a



(portable) self-contained, spring device (Fig. 5) is known as the compression-set (cold flow) for that stock. For stocks softer than 70 A. S. T. M. hardness, a 400-lb. load on discs one square inch in area is recommended.

The test may be conducted in any ordinary Freas-type oven provided with a



Figure 6—Flexometer

fan for circulating the air to assure a uniform temperature. The test clamp should be loaded at the test temperature (*i. e.*, immediately upon removal from the oven). It should be so located in the oven that direct heating is avoided. Tests should be

run in duplicate, one to each clamp, with the test pieces between bright chromium plated surfaces. Test discs should be cut by means of a sharp steel die in an arbor press. Badly cupped or distorted test pieces should be discarded. A more satisfactory but less available, method is to cut out discs by holding a piece of rubber against a tubular, high-speed, rotary cutter.

For accurate work, test pieces must be of the same gage within  $\pm 0.005$  inch. The gage is determined to the nearest thousandth by a standard Randall & Stickney gage with a  $\frac{3}{4}$  inch foot operated by a load of 0.44 lb. (1 lb. per sq. in.). Test pieces should be removed from the clamps immediately upon removal from the oven and placed on a piece of wood for 30 minutes to reach equilibrium. The final gage is then determined at the center of the test piece to the nearest thousandth of an inch by means of a No. 2 B. and S. micrometer. The reading is taken at the moment of contact of the gage feet on the sample with "no pressure." The percentage decrease in gage is then calculated and reported as the compression-set. The above test is intended for check testing between laboratories and for research and development work.

#### Routine Tests on Production Items

A 22-hour cycle will enable an operator to establish a definite time for tests on a number of set clamps and hence is recommended for daily routine or production tests. Comparative data differing only fractionally from the standard are thus secured.

The standard test sample can be obtained from practically all of the common vibration absorbing parts. However, in the case of rubber bonded to metal it is preferable for tests to be conducted on a composite rubber-metal test piece, one inch square, cut from the whole insulator. Other details of the test are the same, it being borne in mind that the gage of the metal does not enter into the calculation of compression-set.

One prominent testing machine company is preparing to offer in the near future a standard compression-set clamp to meet the above test.

#### Dynamic Fatigue Tests

The vibrations intercepted by rubber insulators impose repeated stresses of variable degrees of magnitude on the rubber itself. In some cases in which the frequency of vibration is high and the amplitude is low, the part may be only lightly stressed, particularly when it is not assembled under an original stress. In the case of a spring shackle (or Silent Bloc) the rubber may be highly stressed, both originally and by vibrations or oscillations of considerable magnitude but of moderate frequency. In such parts deterioration tends to develop, due to the heat developed by the repeated dynamic stressing. Some surface wear also eventually occurs.

#### Flexometer Test

The most important laboratory test for evaluating rubber to withstand such service is the Flexometer Test<sup>6</sup> in which the part is repeatedly stressed, either with or without initial assembly load, in a manner simulating service flexure and/or torque. A test piece  $\frac{3}{4}$  inch wide by 1 inch high by  $1\frac{5}{8}$  inch long is assembled between the test plates of the Flexometer (Fig. 6) under 50% compression in "constant deflection" tests, or under 200 lbs. per sq. in. in tests at "constant load," using spring loads. The top plate oscillates 800 times per minute in the direction of the length of the sample. The lower plate may or may not (as desired) oscillate in a rotary manner. The linear amplitude of oscillation of either plate is  $\pm \frac{1}{4}$

inch, although this can be set at will. After a flexing period of 1 or 2 hours, depending on the quality of the stock, the sample is removed and flexure-set is measured following a 30-minute recovery period. Tests may be run to ultimate failure<sup>7</sup> due to excessive heat generated by the stressing, which has not been dissipated. In these tests of failure by blow-out, the test piece is insulated from the metal plates of the Flexometer by replaceable blocks of fine-grained wood. The "blow-out" is signaled by a bell operated by electrical contact when the top plate "drops" onto a terminal, coincident with the softening of the test-piece. The test is so severe that a test-piece changes from a condition of absolutely no porosity or failure to one of complete failure by actual blow-out (melting) in less than one minute at the end of the test.

Other important tests are repeated compression<sup>8</sup> and repeated impact till blow-out,<sup>7</sup> but neither is so flexible nor as severe as the Flexometer Test, which finds its greatest application only to very high quality rubber.

#### References

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- <sup>2</sup> *India Rubber World*, **81**, No. 5, 75 (1930).
- <sup>3</sup> *India Rubber World*, **52**, No. 2, 430 (1915).
- <sup>4</sup> *India Rubber World*, **49**, 11 (1913).
- <sup>5</sup> Abbott, *Ind. Eng. Chem., Anal. Ed.*, **2**, 145 (1930); *RUBBER CHEM. AND TECH.*, **3**, 43 (1930).
- <sup>6</sup> *Ind. Eng. Chem.*, **20**, 853 (1928); *RUBBER CHEM. AND TECH.*, **1**, 503 (1928).
- <sup>7</sup> *J. S. A. E.*, **27**, No. 5, 600 (1930).
- <sup>8</sup> *India Rubber World*, **78**, No. 6, 55 (1928).

# Factors Affecting Rate of Vulcanization of Chloroprene Plastic Polymers

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*The rate of vulcanization of chloroprene plastic polymers and the range of cure and physical properties of the vulcanizates are profoundly affected by the addition of various metallic oxides, sulfur, certain acid softeners, and other organic compounding ingredients. These effects are, in general, not produced except when the above mentioned materials are used in specific combinations with one another.*

THE preparation of chloroprene plastic polymers and their vulcanization to produce elastic rubber-like products have already been described.<sup>1</sup> The purpose of this paper is to show the effect of various compounding ingredients, alone and in combination with one another, on the rate of vulcanization of chloroprene plastic polymers and their effect on the physical properties of the vulcanizates.

All tests reported herein were made on a modified chloroprene plastic polymer (known commercially as DuPrene Type F), containing 94.5 per cent of polymerized chloroprene, 5 per cent of a mineral oil known commercially as medium process oil, and 0.5 per cent of phenyl- $\beta$ -naphthylamine. This modified plastic polymer will be referred to hereafter in this paper, for the sake of brevity, as polymer. All compounded stocks were mixed on a 15  $\times$  30 cm. experimental rubber mill, the temperature of the rolls being maintained at 50° C. Mixed stocks were slabbed off the mill about 0.22 cm. thick and cured in a mold 0.20 cm. thick. All cures

<sup>1</sup> Nieuwland, Calcott, Downing, and Carter, *J. Am. Chem. Soc.*, **53**, 4197 (1931).

were made at 141° C. (286° F.)—the actual temperature of the mold itself.

#### EFFECT OF METALLIC OXIDES

The compounds of Table I were mixed and cured.

TABLE I. COMPOSITION OF COMPOUNDS 504-509

	COMPOUND					
	504	505	506	507	508	509
Polymer	100	100	100	100	100	100
Light calcined MgO	10	...	...	5	5	...
ZnO	...	10	...	5	...	5
Sublimed litharge	...	...	10	...	5	5

TABLE II. PHYSICAL TESTS ON COMPOUNDS 504-509

COM- POUND	CURE AT 141° C.	STRESS AT ELONGATION OF:			TENSILE STRENGTH	ELONGA- TION AT BREAK
	Min.	300%	500%	700%	Kg./sq. cm.	%
504	20	5.3	19.3	43.9	80.9	920
	45	7.0	19.3	43.9	75.6	900
	90	8.8	28.1	58.0	93.2	900
505	20	10.5	33.4	73.8	116	800
	45	8.8	26.4	68.5	144	900
	90	8.8	26.4	93.2	93.2	700
506	20	5.3	19.3	47.5	58.0	780
	45	5.3	15.8	42.2	91.9	900
	90	8.8	26.4	61.5	61.5	700
507	20	3.5	12.3	33.4	75.6	1000
	45	5.3	21.1	47.5	79.1	880
	90	7.0	26.4	56.3	96.7	920
508	20	3.5	10.6	29.9	56.3	920
	45	5.3	14.1	31.6	75.6	960
	90	10.5	33.4	63.3	77.5	780
509	20	5.3	14.1	33.4	84.4	960
	45	5.3	14.1	33.4	86.1	980
	90	8.8	21.1	45.7	118	960

All these compounds contain 10 per cent total weight of metallic oxides based on the weight of the polymer. Physical properties of these compounds cured 20, 45, and 90 minutes at 141° C. are shown in Table II.

The polymer used for these tests can be vulcanized without the addition of any other ingredients, but the vulcanizate is weak, having a maximum tensile strength of approximately 35 kg. per sq. cm. when cured 60 minutes at 141° C. (the optimum cure). The tests shown in Table II demonstrate the beneficial effect of adding metallic oxides but in no case does the vulcanizate have satisfactory physical properties.

Certain compounds were mixed and cured to show the effect of adding grade FF wood rosin (Hercules Powder Company) of the following composition: melting point, 177° F. (81° C.); acid number, 153; and saponification number, 169. The composition of these compounds is shown in Table III.

TABLE III. COMPOSITION OF COMPOUNDS 511-516 AND 518

	COMPOUND						
	511	512	513	514	515	516	518
Polymer	100	100	100	100	100	100	100
Rosin	5	5	5	5	5	5	5
Light calcined MgO	10	...	...	5	5	...	...
ZnO	...	10	...	5	...	5	...
Sublimed litharge	...	...	10	...	5	5	...

Compound 512 scorched during mixing to such an extent that it was impossible to obtain good cures. Physical tests on the other compounds are shown in Table IV.

TABLE IV. PHYSICAL TESTS ON COMPOUNDS 511, 513-516, AND 518

COM- POUND	CURE AT 141° C.	STRESS AT ELONGATIONS OF:			TENSILE STRENGTH	ELONGA- TION AT BREAK
	Min	300%	500%	700%		
		Kilograms per sq. cm.			Kg./sq. cm.	%
511	20	7.0	24.6	61.5	170	1000
	45	12.3	36.9	86.1	174	900
	90	17.6	45.7	118	172	800
513	20	7.0	17.6	47.5	110	860
	45	8.8	24.6	79.1	79.1	700
	90	10.6	33.4	...	65.0	620
514	20	15.8	31.6	84.4	257	950
	45	17.6	36.9	94.9	230	900
	90	17.6	40.4	102	179	820
515	20	7.0	19.3	51.0	167	980
	45	10.6	29.9	87.9	158	830
	90	15.8	38.7	105	123	740
516	20	7.0	12.3	33.4	118	930
	45	8.8	17.6	65.0	123	830
	90	12.3	31.6	93.2	93.2	700
518	60	..	7.0	12.3	43.9	1000
	120	..	8.8	15.8	58.0	1020

The effect of adding rosin has been in every case to increase the rate of cure and substantially improve the physical properties of the vulcanizate. Its beneficial effect is greatest in the compounds containing magnesia, either alone or in combination with other oxides, and is particularly great in the case of compound 514 which contains the combination of zinc oxide and magnesia. That this beneficial effect of rosin is due to its interaction with the metallic oxides is shown by compound 518 which contains rosin alone, and which cures no faster and has no better physical properties than would be obtained from the polymer itself without addition of any compounding ingredient.

Tests on compound 514, which is the best by far in this series, are shown in Table V over a range of cures from 10 to 120 minutes at 141° C.

TABLE V. PHYSICAL TESTS ON COMPOUND 514

CURE AT 141° C.	STRESS AT ELONGATION OF:			TENSILE STRENGTH	ELONGATION AT BREAK
	300%	500%	700%		
Min.	Kilograms per sq. cm.			Kg./sq. cm.	%
10	8.8	15.8	38.7	160	1080
20	15.8	31.6	84.4	257	950
30	17.6	35.2	91.9	220	900
45	17.6	36.9	94.9	230	900
60	17.6	40.4	98.4	190	860
90	17.6	40.4	102	179	820
120	19.3	43.9	107	189	830

The effect of metallic oxides on this polymer may be summarized as follows:

1. Magnesia, zinc oxide, and litharge all accelerate the vulcanization of the polymer and greatly increase the stiffness of the vulcanized products.



2. This effect is much more marked in the presence of rosin or its equivalents. (Equivalents of rosin will be discussed later under the heading "Softeners.")

3. The use of zinc oxide alone is impractical since it promotes vulcanization at low temperatures and hence causes scorching. This is especially true in the presence of rosin.

4. The best results are obtained by using magnesia in conjunction with zinc oxide in the presence of rosin. The combination of these two oxides has far greater effect than either of them alone.

#### EFFECT OF SULFUR

Formulas were mixed and cured (Table VI) to show the effect of adding 0.5 part of sulfur to the compounds of Table I.

TABLE VI. COMPOSITION OF COMPOUNDS 537-540

	COMPOUND					
	535	536	537	538	539	540
Polymer	100	100	100	100	100	100
Light calcined MgO	10	...	...	5	5	...
ZnO	...	10	...	5	...	5
Sublimed litharge	...	...	10	...	5	5
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5

The most striking effect of the addition of this small amount of sulfur is that the compounds containing sulfur all have a marked tendency to scorch during mixing. Compound 536 scorched so badly in spite of all precautions that it was impossible to obtain satisfactory cures. Compounds 537 and 540 were almost as bad as 536 in this respect. Physical tests on the compounds containing magnesia alone and in combination with zinc oxide and litharge are shown in Table VII.

TABLE VII. PHYSICAL TESTS ON COMPOUNDS 535, 538, AND 539

COM- POUND	CURE AT 141° C.	STRESS AT ELONGATION OF:			TENSILE STRENGTH	ELONGA- TION AT BREAK
	Min.	300%	500%	700%		
	Kilograms per sq. cm.				Kg./sq. cm.	%
535	20	10.6	49.2	96.7	121	800
	45	17.6	59.8	111	142	800
	90	19.3	58.0	123	123	700
538	20	10.6	42.2	98.4	98.4	700
	45	17.6	66.8	...	134	680
	90	21.1	73.8	...	94.9	560
539	20	8.8	38.7	82.6	82.6	700
	45	8.8	40.4	94.9	149	860
	90	12.3	54.5	123	146	760

By comparing Table VII with Table II it will be seen that the effect of sulfur has been in each case to accelerate the cure and to increase greatly the stiffness of the vulcanized compounds. It has materially shortened the range of cure of the compound containing magnesia and zinc oxide (compound 538), but this effect is less marked in the case of compounds 535 and 539. However, none of these stocks can be regarded as satisfactory, and even the compounds containing magnesia, either alone or together with zinc oxide or litharge, have some tendency to scorch during mixing.

When sulfur is added to compounds containing the metallic oxides plus rosin, its effect is quite different. In the com-

pounds containing magnesia it has practically no tendency to cause scorching on the mill. It does tend to cause scorching in the compounds containing zinc oxide or litharge alone or the combination of the two but this effect is much less marked than in the compounds containing no rosin. These facts were observed during mixing of formulas (Table VIII) which are the same as those of Table III excepting that 0.5 part of sulfur has been added.

TABLE VIII. COMPOSITION OF COMPOUNDS 542-547

	COMPOUNDS					
	542	543	544	545	546	547
Polymer	100	100	100	100	100	100
Light calcined MgO	10	...	...	5	5	...
ZnO	...	10	...	5	...	5
Sublimed litharge	...	...	10	...	5	5
Rosin	5	5	5	5	5	5
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5

Stress-strain data on these compounds, cured at 141° C., are shown in Table IX. Compound 543 is omitted because, in spite of all precautions, it scorched during mixing to such an extent as to make a physical test of little value.

TABLE IX. PHYSICAL TESTS ON COMPOUNDS 542 AND 544-547

COM- POUND	CURE AT 141° C. Min.	STRESS AT ELONGATION OF:			TENSILE STRENGTH Kg./sq. cm.	ELONGA- TION OF BREAK %
		300%	500%	700%		
		Kilograms per sq. cm.				
542	20	10.6	28.1	63.3	221	1000
	45	12.3	33.4	77.3	190	940
	90	19.3	51.0	132	169	760
544	20	8.8	17.6	45.7	98.4	900
	45	7.0	15.8	47.5	176	1000
	90	10.6	22.9	66.8	153	880
545	10	8.8	21.1	47.5	204	1080
	20	17.6	40.4	98.4	232	920
	45	19.3	42.2	102.0	232	900
	90	19.3	45.7	116	190	840
	120	19.3	45.7	118	185	800
546	10	7.0	14.1	28.1	121	1160
	20	8.8	19.3	47.5	181	1030
	45	10.6	29.9	68.5	183	990
	90	15.8	36.9	91.9	227	930
	120	14.1	36.9	102	223	870
547	20	7.0	14.0	36.9	120	950
	45	8.8	15.8	47.5	174	960
	90	12.3	24.6	68.5	162	880

Compound 542, which contains magnesia but no zinc oxide or litharge, has fairly satisfactory physical properties, but the elongation drops off relatively rapidly on the overcure (90 minutes). Compound 544, which contains litharge alone, is a rather soft and tender stock, but compounds of this type may have commercial value for such purposes as insulated wire where the presence of zinc and magnesia may be objectionable. Compound 546, containing magnesia and litharge, has fairly satisfactory physical properties and an excellent range of cure. Compound 545, containing magnesia and zinc oxide, is stiffer throughout the range of cures, has a flat curing curve, and exhibits high tensile strengths and no tendency toward reversion.

Higher percentages of sulfur produce an even greater increase in the rate of cure and in the stiffness. Tests have been conducted on the compounds of Table VIII with sulfur increased to 2.0 and further to 5.0 parts. The addition of as much as 5.0 parts of sulfur causes the elongation to drop off on overcures. Increasing the sulfur in compound 545 (Table VII) from 0.5 to 2.0 parts causes a slight increase in the rate of cure, the correct cure being reached between 10 and 20 minutes at 141° C., with tensile strength of 3500 pounds per square inch and an elongation of 900 per cent.

The effect of sulfur on this polymer may be summarized as follows:

1. It has a marked tendency to cause scorching in the absence of rosin or its equivalent.
2. Even in the presence of rosin, sulfur tends to cause scorching in compounds containing no magnesia, but compounds containing sulfur in conjunction with both magnesia and rosin have hardly any tendency to scorch and can be mixed without difficulty.
3. In compounds containing no rosin, sulfur tends to cause the elongation to drop off rapidly on overcures, but in the presence of rosin, and especially in the presence of rosin plus magnesia plus zinc oxide or litharge, it does not shorten the range of cure and materially improves the strength and toughness of the vulcanizates over the entire range of cures.

#### EFFECT OF SOFTENERS

The formulas shown in Table X were mixed and cured to show the effect of certain pine products commonly used in rubber compounding.

TABLE X. COMPOSITION OF COMPOUNDS 582-585

	COMPOUND			
	582	583	584	585
Polymer	100	100	100	100
Light calcined MgO	5	5	5	5
ZnO	5	5	5	5
Rosin oil	5	...	...	...
Medium pine tar	...	5	...	...
Rosin	...	...	5	...
Pine oil	...	...	...	5

The rosin oil and pine tar used for these tests analyzed as follows:

	PINE TAR	ROsin OIL
Acid number	68.0	52.7
Saponification value	53.4	10.8
Iodine number	68.2	63.6
Specific gravity at 25° C	1.0341	0.9655

Stress-strain data on these compounds after curing at 141° C. are shown in Table XI.

These tests show that rosin oil materially increases the rate of cure and stiffness of the cured stocks. Pine tar has a similar but somewhat greater effect. Rosin still further increases the stiffness and rate of cure, whereas pine oil has no appreciable effect.

Further tests, not reported in detail in this paper, have shown that turpentine and other pine products, consisting

largely of terpenes, have, like pine oil, little or no effect. However, abietic and certain other aromatic acids are, like rosin, powerful accelerators and stiffeners. On the other hand, stearic and other fatty acids have little or no effect.

TABLE XI. PHYSICAL TESTS ON COMPOUNDS 582-585

COM- POUND	CURE AT 141° C. Min.	STRESS AT ELONGATION OF:			TENSILE STRENGTH Kg./sq. cm.	ELONGA- TION AT BREAK %
		300%	500%	700%		
		Kilograms per sq. cm.				
582	20	7.0	21.1	45.7	151	1080
	45	12.3	31.6	73.8	179	930
	90	17.6	45.7	112	162	800
583	20	7.0	22.8	52.7	137	1000
	45	14.0	43.9	96.7	185	890
	90	19.3	52.7	118	155	780
584	20	15.8	31.6	84.4	237	950
	45	17.6	36.9	94.9	230	900
	90	17.6	40.4	102	179	820
585	20	..	..	7.0	26.4	1040
	45	..	5.3	14.0	40.4	1020
	90	3.5	10.6	22.9	49.2	1000

## EFFECT OF FACTICE AND CUMAR RESIN

The formulas shown in Table XII were mixed and cured to show the effect of adding various proportions of brown factice and *p*-coumarone resin (Cumar RH) to compound 514 (Table II):

TABLE XII. COMPOSITION OF COMPOUNDS 588, 589, 591-593, AND 595

	COMPOUND					
	588	589	591	592	593	595
Polymer	100	100	100	100	100	100
Light calcined MgO	5	5	5	5	5	5
ZnO	5	5	5	5	5	5
Rosin	5	5	5	5	5	5
Brown factice	5	20	20	...	...	...
<i>p</i> -Coumarone	...	...	...	5	20	20
Sulfur	...	...	0.5	...	...	0.5

Compounds 591 and 595 should be compared with compound 545 (Table VIII). Stress-strain data on these compounds are shown in Table XIII.

Comparisons of these tests with those on compound 514 (Table IV) and with the tests on compound 545 (Table IX) show that brown factice has but little effect on the rate of cure, with a slight tendency toward acceleration. Similar compounds containing white factice were also run but are not reported here since the results were substantially the same, excepting that white factice has slightly greater accelerating effect. The addition of 0.5 part of sulfur to the compound containing 20 parts of brown factice (compound 591) increases the rate of cure to about the extent that would be expected from the effect of sulfur in the absence of factice.

Coumarone resin has a distinct softening effect but does not retard the cure even when used to the extent of 20 per cent based on the weight of the polymer. Coumarone has the effect of increasing the elongation and preventing the elongation from dropping off on overcures. The addition of 0.5 part of sulfur had but little effect on the rate of cure of the

compound containing 20 parts of coumarone. In spite of their high elongations the coumarone compounds have quick recovery from extension and low permanent set.

Coumarone is a valuable compounding ingredient for this polymer since it increases the tackiness of the uncured stocks. Factice has the opposite effect, and for this reason it should prove to be beneficial to use these two ingredients in combination with each other. Further tests on the effect of adding coumarone, factice, and other organic fillers, in combination with one another, to chloroprene polymers will be reported in a subsequent paper.

TABLE XIII. PHYSICAL TESTS ON COMPOUNDS 588, 589, 591-593, AND 595

COM- POUND	CURE AT 141° C.	STRESS AT ELONGATION OF:			TENSILE STRENGTH	ELONGA- TION AT BREAK
	Min.	300%	500%	700%	Kg./sq. cm.	%
		Kilograms per sq. cm.				
588	20	12.3	33.4	75.6	229	960
	45	17.6	45.7	109	221	880
	90	19.3	45.7	112	195	850
589	20	15.8	35.2	75.6	186	960
	45	21.1	49.2	116	163	790
	90	22.9	52.7	134	158	740
591	20	17.6	38.7	84.4	170	880
	45	22.9	52.7	121	162	780
	90	22.9	59.8	...	135	690
592	20	12.3	28.1	70.3	216	980
	45	14.1	33.4	86.1	216	920
	90	14.1	35.2	86.1	213	910
593	20	5.3	17.6	38.7	165	1080
	45	10.6	24.6	54.5	193	1000
	90	10.6	24.6	54.5	167	970
595	20	8.8	19.3	45.7	206	1130
	45	10.6	24.6	56.3	197	1000
	90	10.6	26.4	61.5	193	980

#### SUMMARY

These tests have clearly shown the desirability of compounding this polymer with zinc oxide, magnesia, and rosin, and have demonstrated that these three ingredients when used together have a desirable effect that cannot be obtained with, or even predicted from, the results obtained with any one of them alone or the combination of any two of them. It has been shown further that, although it is possible to obtain good vulcanized products from this polymer without the addition of sulfur, a great increase in the rate of cure and substantial improvement in physical properties of vulcanized products result from the use of as little as 0.5 per cent of sulfur on the weight of the polymer. It is further shown that pine tar and rosin oil may be substituted for rosin but that they are somewhat less efficacious. The authors postulate that the value of rosin, pine tar, and rosin oil is probably due to the organic acids that they contain. Coumarone resin and brown factice are shown to be desirable compounding ingredients for chloroprene polymers.

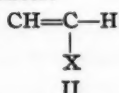
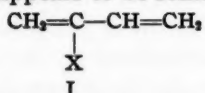
Presented before the Division of Rubber Chemistry at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

[CONTRIBUTION NO. 107 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT  
DE NEMOURS & Co.]

## Acetylene Polymers and their Derivatives. V. The Polymerization of Bromoprene (Third Paper on New Synthetic Rubbers)

BY WALLACE H. CAROTHERS, JAMES E. KIRBY AND ARNOLD M.  
COLLINS

Chloroprene (I, X = Cl) polymerizes spontaneously to yield a rubber-like product,<sup>1</sup> and the speed of this transformation is roughly 700 times greater than the analogous transformation of isoprene. The present paper deals with the behavior of bromoprene<sup>2</sup> (I, X = Br), and the results may be summarized in the statement that it shows no significant qualitative differences from chloroprene, although its speed of polymerization under most conditions appears to be somewhat greater.



In connection with the behavior of these materials the following analogies are of interest. Vinyl chloride and vinyl bromide (II, X = Cl and Br) polymerize spontaneously yielding products of very high molecular weight,<sup>3</sup> but this behavior is not shown by propylene, which polymerizes only in the presence of special catalysts or under drastic conditions and then yields products having only moderately high molecular weights. The haloprenes (I) bear the same structural relationship to isoprene that the vinyl halides bear to propylene. Thus the very powerful activating effect of a single halogen atom on ethylene is also manifested in butadiene (when the halogen atom is on the  $\beta$ -carbon). The rate of polymerization is of great importance in studying the behavior of dienes since a high rate not only makes it possible to obtain experimental results in a reasonable length of time, but it permits one to extend the observations over a wide range of conditions. It becomes possible then to recognize the different types of reactions involved in the spontaneous polymerization and to obtain data on the way in which these different types of reactions are affected by changes in the conditions. Data of this type on chloroprene have already been presented, and it will be useful to review them briefly (with some extensions) and to make comparisons with those now available for bromoprene and for other dienes.

The polymerization of chloroprene leads to the four well defined and qualitatively distinct types of polymers shown in the chart.

(1) Carothers, Williams, Collins and Kirby, *This Journal*, **53**, 4203 (1931).

(2) Carothers, Collins and Kirby, *ibid.*, **55**, 786 (1933).

(3) Staudinger, Brunner, and Feisst, *Helv. Chim. Acta*, **13**, 805 (1930).





The  $\beta$ -polymer, a terpene-like material, is an undesirable by-product in the rubber synthesis. In the chloroprene polymerization the production of  $\beta$ -polymer becomes appreciable only at temperatures higher than are necessary to bring about a rapid formation of  $\alpha$ -polyprene. Butadiene, isoprene and dimethylbutadiene polymerize very slowly; to get the transformation to proceed at a reasonable rate, elevated temperatures are generally used, and this results in the formation of relatively large amounts of  $\beta$ -polymer.

The  $\omega$ -polychloroprene is also a useless product; it is made up of discrete rubber-like particles (irregular globules) which are non-plastic and not even swelled by rubber solvents. The formation of this polymer is autocatalytic. When a speck of the  $\omega$ -polymer appears (or is introduced) in a specimen of incompletely polymerized chloroprene, the entire specimen is soon more or less completely converted into the  $\omega$ -polymer. The formation of nuclei of the  $\omega$ -polyprene is favored by strong ultraviolet light and by metal surfaces (*e. g.*, sodium, potassium, mercury, iron, copper and aluminum). The opportunities for the formation of such nuclei are also increased by a long reaction time under any particular set of conditions. Similar polymers, frequently described as cauliflower-like masses, have been obtained from isoprene, butadiene and dimethylbutadiene, and one suspects that they may be the forms in which the polymers of these dienes are most frequently obtained. The very slow rate of the polymerization of these dienes would be especially favorable to the formation of  $\omega$ -polymer.

The term rubber-like is vaguely used to cover a multitude of the most diverse properties, and the literature of synthetic rubber is exceedingly obscure. Most of the agencies that are available to hasten the very slow polymerization of isoprene and butadiene are such as have been found in the case of chloroprene to affect more strongly the conversion of the  $\alpha$ - into the  $\mu$ -polymer than the formation of the  $\alpha$ -polymer. One may expect therefore that the isolation of a true  $\alpha$ -polyprene<sup>4</sup> from the isoprene and butadiene products will present especial difficulties. So far as we are aware no clear disclosure has ever been made of an  $\alpha$ -polyprene from isoprene or from butadiene. However, when isoprene is subjected to a pressure of 12,000 atmospheres until 30% of the isoprene has polymerized, the polymer is at least 90% soluble in ether.<sup>5</sup> If the reaction is allowed to proceed further until 80% of the isoprene has polymerized, the product is completely insoluble.<sup>5,6</sup> Thus the formation of a completely vulcanized

(4) With the aid of swelling agents, softeners, and lubricants it is possible to confer a certain amount of plasticity on  $\mu$ -polychloroprene. It is also possible to obtain from chloroprene plastic polymers that, on being heated, lose their plastic properties very incompletely or not at all. The material that we refer to as  $\alpha$ -polychloroprene is an inherently plastic, *polymerisable* polymer; its plastic properties are completely lost and its elastic properties become fully developed when it stands or is heated.

(5) Conant and Tongberg, *THIS JOURNAL*, **52**, 1667 (1930).

(6) According to observations made by Dr. H. W. Starkweather in this Laboratory, isoprene polymers prepared in this manner are also completely non-plastic.

rubber-like product without the aid of sulfur is by no means peculiar to chloroprene. In fact the differences between the behavior of chloroprene and the behavior of other dienes appear to be differences of degree rather than differences of kind.

**The Spontaneous Polymerization of Bromoprene.**—A sample of bromoprene when allowed to stand at the ordinary laboratory conditions in a stoppered flask containing a small amount of air becomes noticeably more viscous after twelve to fifteen hours. As the reaction proceeds, the viscosity increases; after about five days the sample sets to a stiff, elastic jelly containing a considerable amount of unchanged bromoprene. Usually after eight to ten days all of the bromoprene has reacted, but the time required varies considerably in different experiments. The product has a density of about 1.74, and this is 24% greater than the density of the bromoprene. (The increase in density in the formation of  $\mu$ -polychloroprene is about 28%.)

This product,  $\mu$ -polybromoprene, corresponds in its properties with the  $\mu$ -polychloroprene already described. It is tough, resilient, and elastic but harder than the analogous product from chloroprene. On standing it gradually undergoes further change: it becomes still harder and less extensible and the resemblance to soft vulcanized rubber pretty largely disappears although it still remains very tough and retains considerable elasticity and resiliency. These changes in the nature of the product are due, at least in part, to a progressive action of air and they can be retarded by the application of antioxidants to the surface of the sample.  $\mu$ -Polybromoprene is similar to  $\mu$ -polychloroprene in its behavior toward solvents. It is greatly swelled by chloroform, carbon tetrachloride and aromatic hydrocarbons but remains practically unchanged after prolonged immersion in alcohol, ether, or aliphatic hydrocarbons such as gasoline.

**$\alpha$ -Polybromoprene.**—The preparation of an  $\alpha$ -polybromoprene (plastic polymer) presents no difficulties. A sample of bromoprene was exposed to light from a Cooper-Hewitt lamp at 25°. After twenty-four hours 50% of the material had been converted into polymer. (This rate is about 40% greater than that usually obtained with chloroprene under the same conditions.) The product was an exceedingly viscous, yellow sirup. When it was mixed with a large volume of alcohol the  $\alpha$ -polybromoprene was precipitated as a soft, plastic mass. This product showed no tendency to resist permanent deformation and sheeted out very readily on cold rolls. Two per cent. of phenyl- $\beta$ -naphthylamine was worked into the plastic mass to prevent spontaneous conversion into an elastic polymer.<sup>7</sup> The sample was compounded with about 5% of its weight of zinc oxide and heated in a mold at 120 to 125° for twenty minutes. The product was non-plastic, strong, resilient and extensible (500 to 700%). However,

(7) Ref. 1, p. 4219.

compared with a similar product from chloroprene it was somewhat lacking in snap, and its permanent set was rather high. It also showed a greater tendency to "freeze." After about two hours at ordinary temperatures it became very stiff, but the original pliability was restored when it was heated to 80° for a few minutes.

**The Polymerization of Bromoprene in Aqueous Emulsion.**—Like chloroprene, bromoprene is readily dispersed in water and the resulting smooth emulsion polymerizes with great rapidity to form a stable latex. The preparation and polymerization of such an emulsion is illustrated in the following example.

Twenty-five cubic centimeters of 2% aqueous sodium oleate in a wide-mouthed bottle was surrounded by a bath of ice and water. Two drops of triethanolamine was added to the solution, and then, with vigorous stirring, 25 g. of bromoprene. A smooth, milk-like emulsion resulted. After the mixture had stood in the ice-bath for five hours an aliquot portion was removed and poured into a large volume of alcohol. The weight of the precipitate thus obtained indicated that 78% of the bromoprene had polymerized. Under the same conditions chloroprene is only about 20–30% polymerized. The bromoprene emulsion described above was transferred to a refrigerator. After seventeen hours, more than 95% of the bromoprene had polymerized. Five cubic centimeters of 3% ammonium hydroxide was added to stabilize the emulsion and a small amount of an aqueous dispersion of phenyl- $\beta$ -naphthylamine (2% on the rubber content) added to function as an antioxidant. The resulting latex was very stable.

As in the case of polychloroprene, the dispersed particles in the synthetic latex derived from bromoprene correspond more closely to the  $\mu$ - than to the  $\alpha$ -polymer. Nevertheless, when the latex is coagulated by the addition of acids, the particles coalesce and cohere very firmly. The coagulum is at first soft and plastic, but it quickly becomes tough, elastic and non-plastic. Homogeneous, coherent films are obtained by allowing the water to evaporate from a thin layer of the fluid latex on a plate of porous porcelain. The films are readily stripped from the plate and the removal of the water can be completed by drying them for a few hours in an oven at 80°. Such films are exceedingly tough and more resistant to tearing than analogous films prepared from chloroprene latices. A typical specimen had a breaking strength of 160 kg./sq. cm. and an elongation at break of 740%. (The elongation of similar polychloroprene films is usually about 800%.) The films exhibited the high permanent set and the tendency to freeze or stiffen already referred to in connection with the vulcanized  $\alpha$ -polybromoprene. Like the latter, they were non-plastic and did not dissolve but merely swelled in chloroform and benzene.

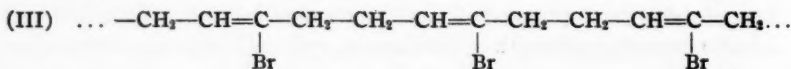
**$\beta$ -Polybromoprene.**—The conversion of bromoprene into a volatile liquid polymer ( $\beta$ -polybromoprene) occurs under conditions similar to those already described for chloroprene.<sup>8</sup> A sample of bromoprene containing about 5% of thioldiphenylamine, a substance which powerfully inhibits the conversion of the haloprenes to rubber-like polymers, was

(8) Ref. 1, p. 4211.

heated in a sealed tube at 80° for five days. When the resulting black oil was poured into alcohol a small amount of a black tar separated. From the alcohol there was obtained by distillation a small amount (about 15%) of a yellow oil boiling at 104 to 110° at 11 mm. It had a fragrant, terpene-like odor very similar to that of  $\beta$ -polychloroprene and was a mild lachrymator. It showed no tendency to polymerize further.

**$\omega$ -Polybromoprene.**—The formation of  $\omega$ -polybromoprene, like the formation of  $\omega$ -polychloroprene, occurs under conditions which result in very slow polymerization. For example, samples of bromoprene containing 0.2% of phenyl- $\beta$ -naphthylamine or 0.5% of tetramethylthiuram disulfide and 0.3% of sulfur slowly became more viscous and, after two to six weeks, a white deposit having a crystalline appearance began to form. After formation of this substance had started, conversion of the whole mass was complete in a few days. The product turned dark brown in color on standing in air.  $\omega$ -Polybromoprene is soft, opaque and non-coherent, while  $\omega$ -polychloroprene is a mass of glistening, hard, rubbery granules. Like  $\omega$ -polychloroprene, it is not swelled by benzene.

**The Structure of Polybromoprene.**—Evidence has already been presented for concluding that  $\alpha$ -polychloroprene is precisely analogous to natural rubber in its chemical structure. The analogies between polychloroprene and polybromoprene are sufficiently close to justify the assumption of a similar structure (III) for the latter compound. The x-ray evidence is especially interesting. The fact that  $\mu$ -polychloroprene when stretched furnishes a fiber diffraction pattern has already been disclosed.<sup>1</sup> Polybromoprene shows a similar behavior, but it furnishes an even sharper pattern (Fig. 1).<sup>9</sup> So far as we are aware, it has not been possible to obtain fiber diagrams from any other synthetic rubbers, and this fact perhaps justifies the conclusion that polychloroprene and polybromoprene are more regular in their molecular structure than any other known synthetic rubbers.



### Summary

The polymerization of bromoprene is closely analogous to that of chloroprene, but somewhat more rapid. Spontaneous polymerization yields as the final product  $\mu$ -polybromoprene, which resembles vulcanized rubber but is more dense than rubber or  $\mu$ -polychloroprene. A plastic ( $\alpha$ ) polybromoprene is readily isolated from partially polymerized bromoprene, and it is converted to the  $\mu$ -product by the action of heat. At elevated temperatures in the presence of inhibitors a volatile liquid ( $\beta$ ) polymer is

(9) The x-ray data will be discussed in more detail in a future paper by Dr. A. W. Kenney.

formed.  $\omega$ -Polybromoprene, a granular, insoluble, rubber-like mass, is produced under conditions that lead to very slow polymerization.

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